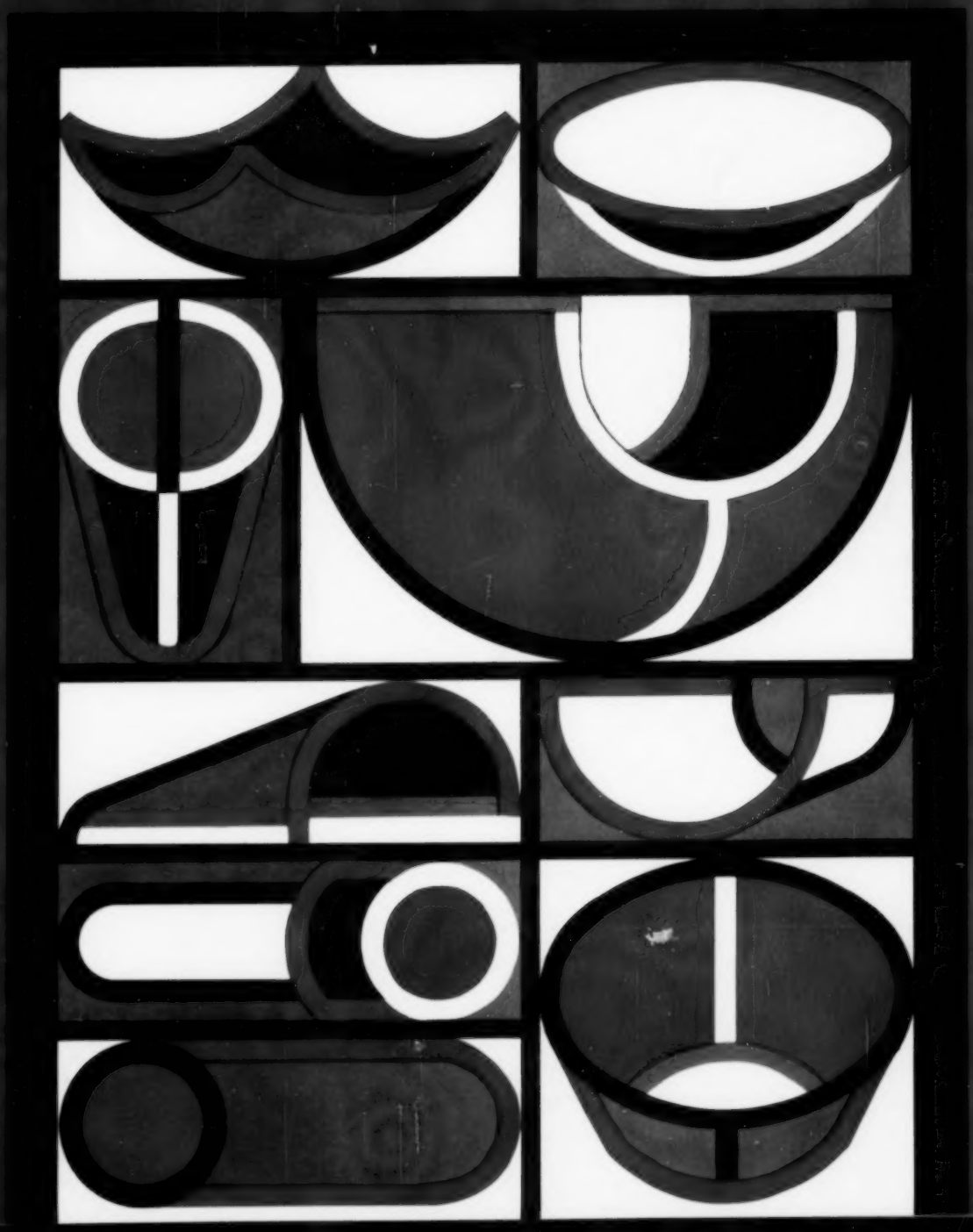
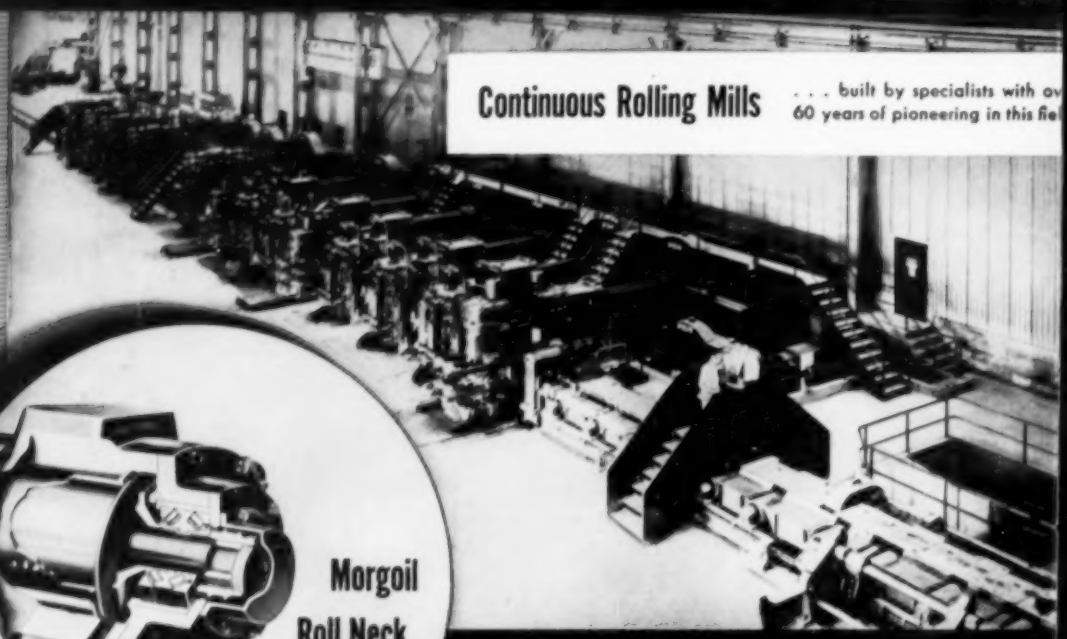
JOURNAL OF

METALS

MAY 1956

IN TWO SECTIONS — SECTION ONE





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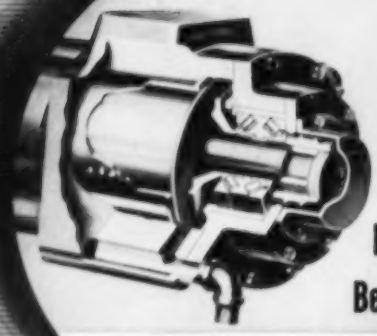

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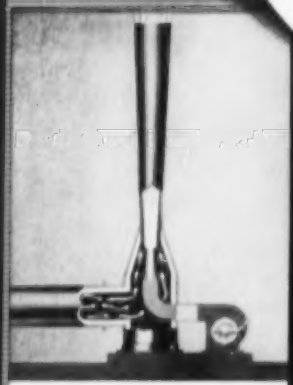

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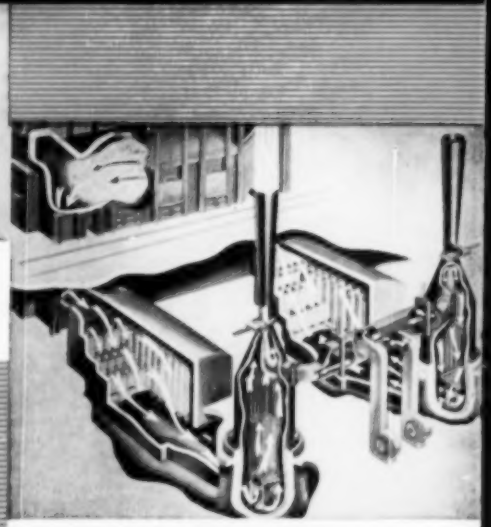

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JOURNAL OF

METALS

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The AIME Publishes:
Journal of Metals
Mining Engineering
Journal of Petroleum Technology

VOL. 8, NO. 5 MAY, 1956

COVER

Strange shapes played a vital part in the construction of the first zirconium vessel for HRT reactor application. Forming, together with newly developed welding techniques, made possible this unique pressure vessel. The story of the design, methods development, and assembly projects is revealed in the article beginning on page 648.

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This issue of JOURNAL OF METALS is in two Sections:
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Engineers. (a) Metallurgist, with advanced degree and knowledge of high temperature reactions and slag-metal systems in electric furnaces, foundry experience grey iron or steel, to carry out metallographic examination, physical testing, prepare reports and sales literature, and visit customers for plant tests. (c) Research Chemist or Metallurgist, B.S. or M.S., for research on gas-solid reactions such as nitriding and bench-type research rather than process development, and an interest in kinetics and rates of reaction helpful. (d) Petrographer, preferably with M.S. and several years experience in petrographic and mineralogical analysis, for examination, identification, and anlysis of ceramic products by physical methods, including X-ray, petrography, and petrographic microscope. Salaries open. Location, western New York State. W3145.

Foundry Superintendent, graduate metallurgist, 30 to 40, for new foundry, ferrous and nonferrous metals. Will be in complete charge under general manager. Company will pay moving expenses and negotiate placement fee. W-3122(a).

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(Continued on page 624)

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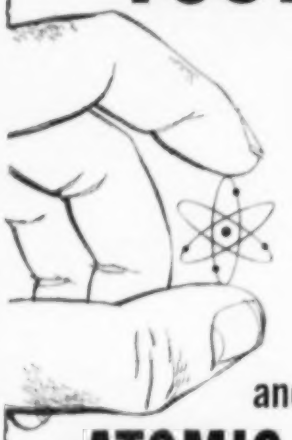

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(Continued from page 622)

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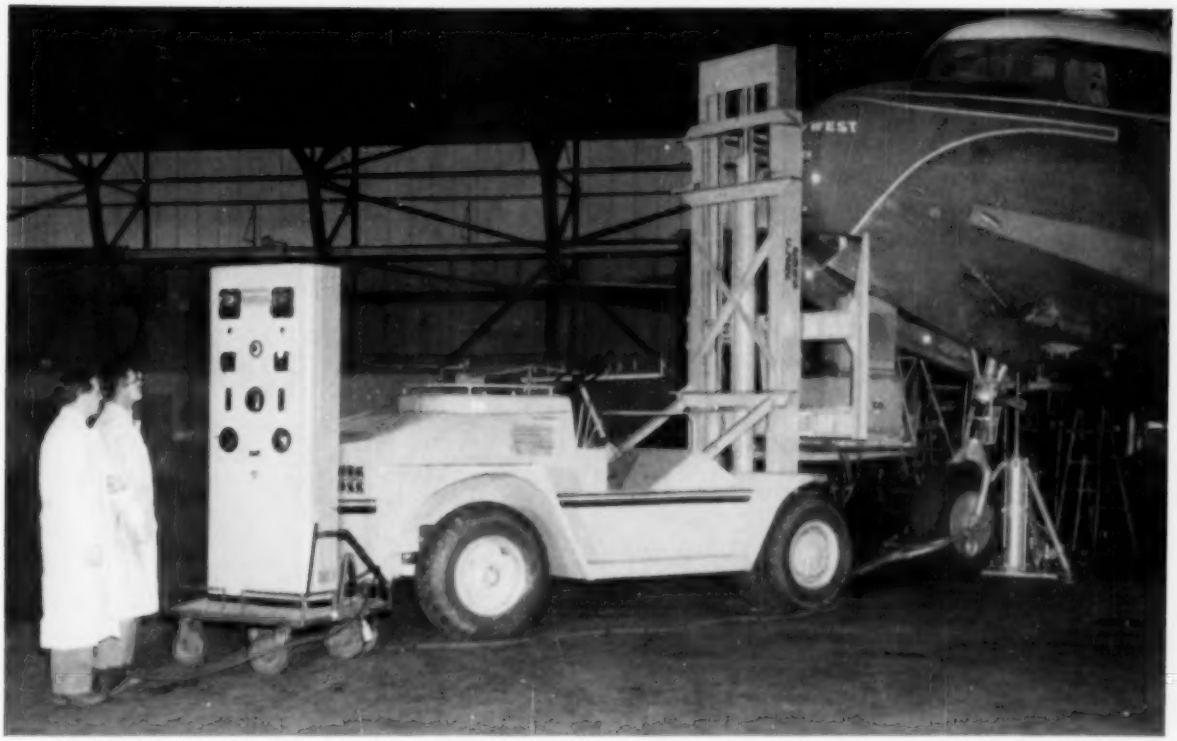

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Books for Engineers

Steel Designers' Manual, by Charles S. Gray and others, *Frederick Ungar Publishing Co.*, $12.50, 909 pp., 1955.—This manual for use by the practicing designer includes advanced methods as applied to modern steel framed buildings and complete data, tables, and diagrams. Sections cover theory, design, and deflection of beams, structural analysis, bunkers and hoppers, foundations, plate girders, properties of sections, etc.

Elevated-Temperature Properties of Carbon Steels, Special Technical Properties No. 180, *ASTM*, $3.75, 63 pp., 1955.—Presented in graphical form and supplemented by data sheets are such pertinent data for steel producers as tensile and yield strength, elongation and reduction of area, stresses for creep rates of 0.0001 and 0.00001 pct. per hr. and rupture strengths for 100, 1,000, 10,000 and 100,000 hr. This information is given for killed carbon steel, ASTM A201 Grade B plant steel, ASTM A106 Grade B pipe steel, killed carbon steel, aluminum killed steel, open steel (rimmed or capped), and other carbon steels.

Atomic Energy Guidebook, edited by Walter A. Shead, *Callahan and Hollowell*, $7.50, July 1955.—Designed as a comprehensive sourcebook covering every phase for civilian use in the atomic energy field, the Guidebook is divided into three sections that deal with atomic energy from the mining of uranium through its end uses. The three sections treat these topics: entering the atomic energy business, which includes a special article by E. N. Trapnell; basic information on the status and future of atomic energy, with an article on the future of atomic energy by E. M. Zuckert; and a six-part directory, which includes state listing, an alphabetical index of companies manufacturing atomic instruments, and of access permit holders, and guides to members and officials of the AEC, citizens committees appointed by the AEC, and statutory committees appointed by congress. The Guidebook contains 30 articles and the directory section.

Engineering Economics and Practice, by Max J. Steinberg and William Glendinning, *W. Glendinning*, $3.00, 114 pp., 4th edition, 1955.—Designed for a two-fold purpose, the book is a summary of accepted theory and practice for engineers preparing for professional examinations and a reference manual for those already practicing. Included among the subjects covered are compound interest formulas, depreciation, comparison of alternate proposals, replacements, and costs. Questions and solutions from Part III, New York State examinations, supplement test materials given.

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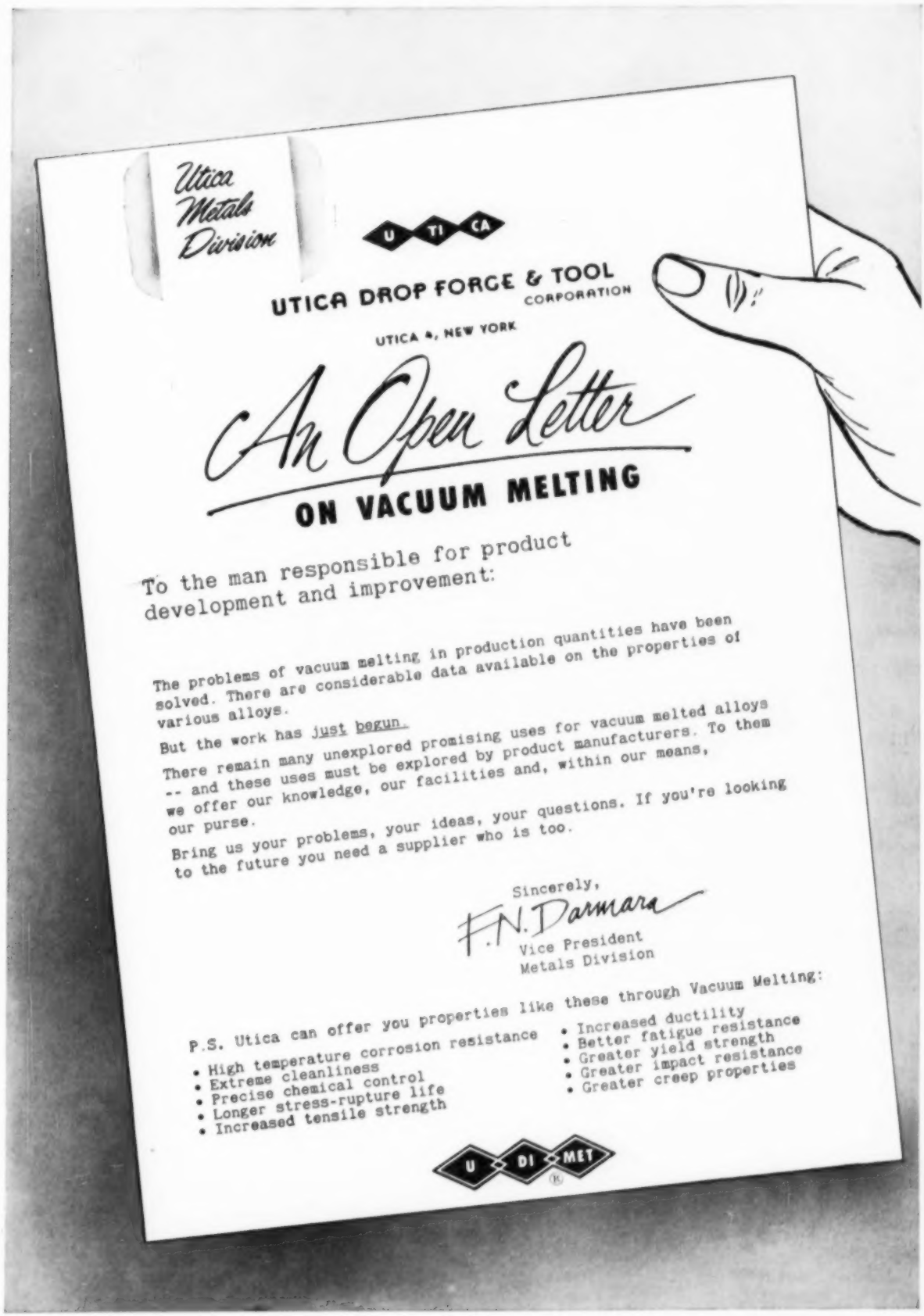
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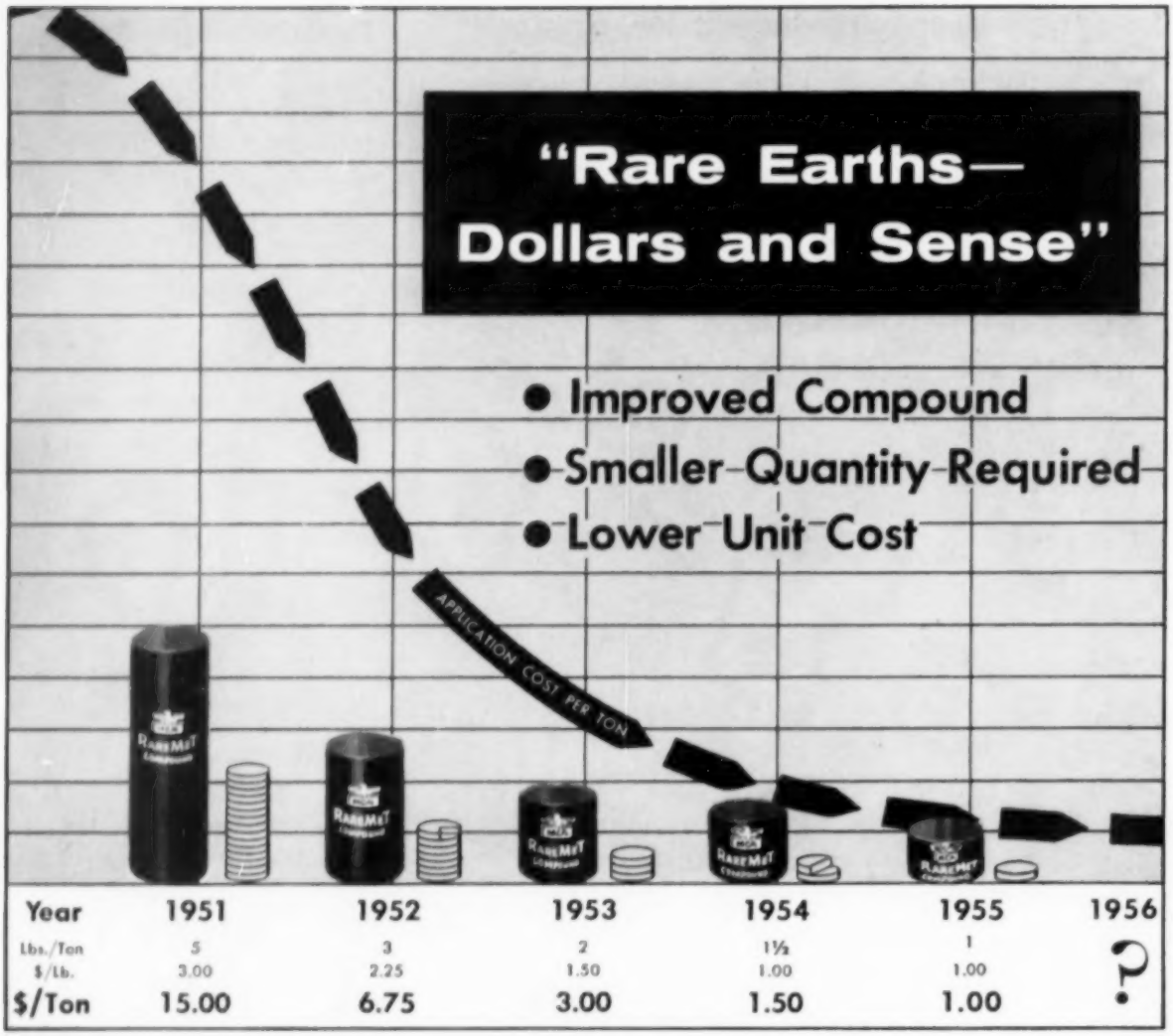

Year	1951	1952	1953	1954	1955	1956
Lbs./Ton	5	3	2	1½	1	
$/Lb.	3.00	2.25	1.50	1.00	1.00	
$/Ton	15.00	6.75	3.00	1.50	1.00	?

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REPORTER

Ample Supplies of Lower-cost Zirconium Foreshadowed by AEC Contract

The AEC has announced the award of five-year supply contracts totaling 11 million lb of reactor grade zirconium for the Navy and the AEC reactor programs. Each of the three recipients will construct a plant with sufficient capacity to supply both AEC and commercial needs. With certain new process developments a reduction in the price of reactor grade zirconium from the current $12 to $14 a lb to some $6 to $7 a lb is foreseen.

U. S. Industrial Chemicals Co., (Div. of National Distillers Products Corp.) plant under construction at Ashtabula, Ohio will use a sodium reduction process to supply AEC 1 million lb annually. NRC Metals Corp., a subsidiary of National Research Corp., using a new purification process, will supply 0.7 million lb a year from a projected plant adjacent to zirconium sand deposits at Pensacola, Fla. Carborundum Metals Co., utilizing the conventional Kroll process developed by AEC, will supply 0.5 million lb annually from a plant to be built at Parkersburg, W. Va. Carborundum is also stepping up AEC deliveries from its Akron, N. Y., plant to 0.325 million lb annually.

At the same time, U. S. Bureau of Mines pilot zirconium plant at Albany, Ore., will be reactivated by August to turn out 0.3 million lb annually. This plant will be operated by Wah Chang Corp. Additional supplies will be met from Japanese exports amounting to 0.2 million lb.

Titanium Capacity Continues to Climb

With the output of titanium sponge increasing spectacularly from 3 tons in 1948 to 7200 tons in 1955, the 1956 production is expected to be some 13,000 tons. The high strength, light weight, and corrosion resistant properties make the metal excellent for use in jet aircraft, ballistic missiles, and atomic installations, which account for at least 90 pct of present consumption. But as the cost of the metal decreases there is an expanding array of nonmilitary uses.

In order to meet these demands Electro Metallurgical Co. has recently put into operation a 7500-ton titanium reduction plant near Ashtabula, Ohio. This plant, using a sodium reduction process, is the largest in the country and the first commercial U.S. producer of titanium by a method other than magnesium reduction.

At the same time, a leading titanium producer, Titanium Metals Corp. of America, has announced plans for expanding capacity at the Henderson, Nev., plant from 3600 to 6000 tons to be in operation late this year. In 1950 TMCA, which is jointly owned by National Lead Co. and Allegheny Ludlum Steel Corp., began conversion of the former Basic Magnesium Plant with the assistance of a $15 million government loan. Titanium ingots produced at Henderson, Nev., are processed into mill products at Allegheny Ludlum plants.

Drift of Things

Regional Meetings Broaden Viewpoint

THIS month members living in the Northwest and those who could travel out there had an opportunity to take a look at the whole of the mineral industry picture. May 3 to 5 marked AIME's Fifth Pacific Northwest Regional Metals and Minerals Conference. What is significant about this meeting, aside from the high caliber of the papers, is that this is a meeting place on a regional basis for technical interests in two branches—Mining and Metals.

Again, in September, those members in the Rocky Mountain province and those who can go out there will have another of these opportunities to see the large picture. This occasion will be the Rocky Mountain Minerals Conference on September 26 to 28 at Salt Lake City. Those guiding the gathering stress that interests covered will cut across the fields of Mining, Metals, and Petroleum. Last year the sessions at this conference were set up on topics of joint interest, drawing men from all technical divisions into discussion of common problems.

This process of cross fertilization has its surprises, some of which show up during discussion. Men in diverse fields are often hacking away at a problem without knowing that they are on opposite sides of it. Meetings organized on a topic or regional basis are the place to find this out.

It is far from new to use common problems to draw men of varied specialization into joint discussion. Certainly the title of one of the Iron and Steel Div.'s conference committees is a case in point: Blast Furnace, Coke Oven, and Raw Materials. In addition to this range of interests, there is the Open Hearth Committee meeting simultaneously with the BFCO&RM group at an annual spring conference. This particular meeting gives participants a chance to take a look at the whole field of iron making—from coal, limestone, and iron ore down to the final ingot.

The preliminary announcement for the AIME Northeastern Mining Branch Conference at Hershey, Pa., November 8 to 10 shows the same kind of thinking. The early information is that the technical program at Hershey will be "comprehensive, branchwide."

Still another approach to this problem is evidenced by the annual Electric Furnace Conference, set this year for December 5 to 7 in Chicago. Here the process is the topic, and again the specialized problems fit into a broad economic and industrial framework.

Looking Ahead for the Institute

In June, MINING ENGINEERING will carry the report of the AIME Long Range Planning Committee, together with some explanatory material and comment. Copies of this report are available now for those who write to headquarters in New York. We wish to stress the importance of the questions this type of planning raises, and hope that every reader will take a close look at the report when it appears in June. Looking far ahead is something that individuals and organization do all too seldom, and this underlines the importance of those times when it is done.

In a way this report on long range planning might be termed: "the engineer looks at his professional engineering society." The same issue will also carry something of a different nature that might be termed: "the engineer looks at his profession." Of this, more below.

Professionalism and the Engineer

Some time ago Engineers Joint Council (of which AIME is a member), charged a committee with the task of studying professional employment conditions and preparing information for employers on the effect of various factors on the development of a truly professional outlook by engineers. This work has resulted in a report now being released by the EJC Board, entitled "Professional Standards and Employment Conditions."

One benefit, at least, of the shortage of engineers—or if one wishes, the lack of an oversupply of engineers—is that the profession and members of the profession are getting more attention both within and without the field than ever before. For once the vital role played by the profession is being recognized by management, by educators, and by the public.

Benefit to the profession is almost certain to flow from this increased notice and attention. Among the hoped-for gains: better training for engineers, more recognition, more financial recognition, and particularly, a stronger professional spirit. This EJC report should help in several of these areas. At least some observers feel that now is the time to capitalize on a favorable situation and raise the stature of engineering as a profession, and to encourage the growth of professionalism, particularly among the younger practitioners.

Employers will play a role in this growth of engineering, it is felt, particularly since many are now searching for other solutions to their professional manpower problems than merely raiding their competitors. Management in many cases appears eager to find assistance and answers as to problems of proper treatment of professional level employees. Several firms have received rude shocks when staff attitude toward the company was revealed through questionnaires.

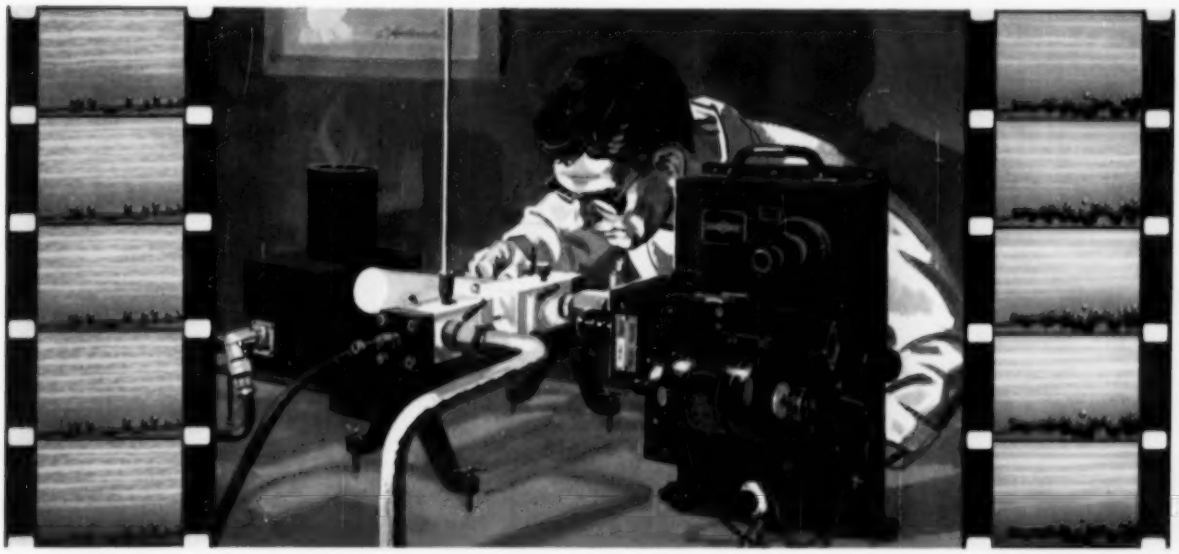
When one large firm moved a laboratory it was jarred to find how few of its people moved with the lab. Money was not the problem. Checkbacks on the people who left revealed big areas of dissatisfaction. Lack of recognition was a sore point, as was lack of a clear picture from the company of where they fitted into its overall operations.

Everyone—government, business, or college—is looking for engineers right now. Out of this search are not only going to come constructive action for the future, but much closer attention to what is now available—to the conserving of the available professional engineering manpower resources they do have.

R. A. Beals

Notable Achievements at JPL

HIGH SPEED PHOTOGRAPHS OF NUCLEATE BOILING were first taken at JPL using a special camera fitted with a Kerr cell shutter. Sequence photos, taken at speeds up to 20,000 frames per second, were the first series of high-speed, high-resolution motion pictures to successfully stop the action of nucleate boiling.



Pioneers in Rocket Motor Heat Transfer Research

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As a result of knowledge gained from the high speed photos and from subsequent work, the role of bubble dynamics has been incorporated into theories of nucleate boiling heat transfer which is the principal mode of heat transfer encountered in the regenerative cooling of liquid propellant rocket motors.

Because of the very high temperatures encountered in propellant combustion, JPL has been engaged in a broad program studying various modes of heat transfer. Emphasis has been placed on studies of boiling heat transfer to liquids, turbulent boundary layer heat transfer to deLaval nozzles, nonsteady heat transfer due to oscillatory flow, and heat transfer with chemical reaction in the boundary layer and on the surface.

The influence of chemical effects is one of several programs that has benefited from the association of talents and experimental techniques from several different fields of specialization. The broad and varied programs, ranging from laboratory experiments to responsibility for missile flight testing, have created unique working conditions for our technical personnel.

Here, at JPL, the research engineer enjoys, to an unusual degree, the stimulus of practical application coupled with an academic atmosphere. If you are interested in such problems and working conditions, we would like to hear from you.

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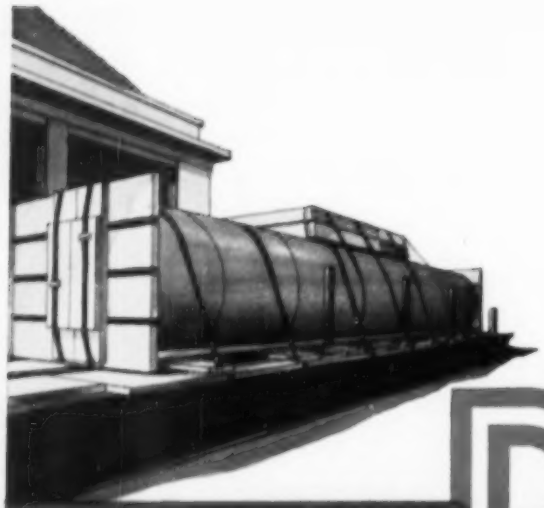

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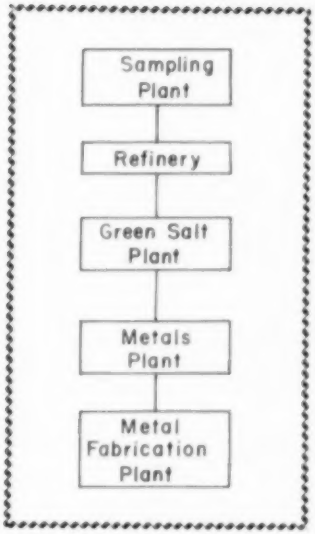
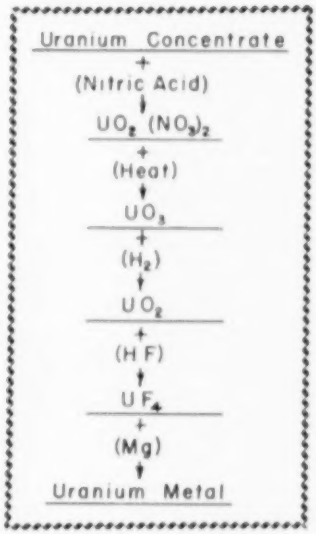
Production of Uranium Metal



Industrial scale output of uranium fuel elements necessitates complex processing to meet specification for atomic reactors.

Fig. 1, left, is a simplified production flowsheet designed to accommodate the chemical flowsheet at right, Fig. 2.



by D. S. Arnold, C. E. Polson,

and E. S. Noe

REACTORS of today and tomorrow require a high uniformity of their fuel elements despite the wide variety of uranium raw materials from the far corners of the earth. To meet these quality standards metallurgists have been working to design production methods capable of yielding reactor feed materials whose maximum impurities are specified in parts per million, whose physical limits are expressed in thousands of an inch, and whose density variations are less than 1 pct.

Such requirements are necessary to maintain normal neutron flow in the atomic reactor and to insure that the isotopic content of the feed material is maintained within narrow limits.

Receiving and Sampling

Uranium ores and concentrates are produced in many sections of the world, including the Belgian Congo, South Africa, Australia, Canada, and the Colorado Plateau of the U. S. Ores from many of the larger deposits are relatively low grade, and these are concentrated near the mine site before shipment to refining centers, but high grade ores may be shipped directly to refineries.

These feed materials, received at the sampling plant in steel drums, are dried, milled, weighed, sampled, and analyzed as necessary for purchasing and process control considerations. Conventional methods are used except for the application of a higher degree of precision in measurements.

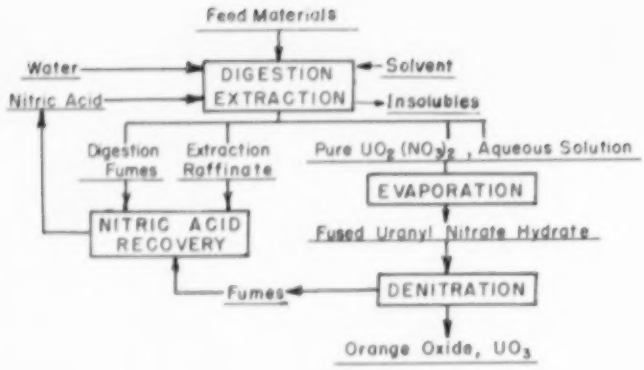
D. S. ARNOLD, C. E. POLSON, and E. S. NOE are with the National Lead Co. of Ohio, Fernald, Ohio.

The various virgin feed materials, i.e., ores and concentrates, are blended among themselves and with materials produced in the metal recovery plant from scrap and reject fractions. Processing takes place according to the flowsheet, Fig. 3.

Recovery and Purification of Uranuim

The uranium content of the feed materials is converted to soluble uranyl nitrate by digestion in nitric acid. The resulting slurry, consisting of acid insolubles and a digest liquor of metal nitrates and excess nitric acid, is pumped into pulsed perforated-plate liquid-liquid extraction columns in which the uranyl nitrate is preferentially extracted by a solvent mixture of tributyl phosphate and kerosene. Purification of the uranyl nitrate in the solvent extract stream from this primary extraction column is accomplished by a partial re-extraction or scrubbing of uranyl nitrate with water in a second pulsed perforated-plate column. The aqueous stream from this second column (scrub column) is recycled or refluxed to the top of the primary extraction column for uranium recovery. The purified uranyl nitrate is recovered from the organic solvent stream from the scrub column by re-extraction with pure water in a third pulsed perforated-plate strip column. The *stripped solvent* stream is recycled to the primary extraction column through a solvent treatment and storage system.

While the uranyl nitrate in the aqueous product meets chemical purity specifications (subsequent processing in general results in product contamination), the uranium is converted through a series of steps to anhydrous uranium tetrafluoride (UF_4), which is used for production of uranium metal by a thermite-type reduction. These steps include evaporation of the uranyl nitrate solution to produce a molten salt of uranyl nitrate hydrate, which is converted to orange oxide (UO_3) by calcination.



Elimination of impurities to produce pure uranium oxide is a key step in producing the metal. The simplified refinery flowsheet is shown in Fig. 3 together with the nitric acid recovery plant, which is essential to the economics of the process.

■ ■ ■

Nitric Acid Recovery: Because of the high cost of nitric acid compared with the other commercial acids, and because of the atmospheric and water pollution problems associated with disposal of nitrate and uranium feed material, operation of nitric acid recovery plant is justified. Facilities include equipment for evaporation of the residual free nitric acid from the raffinates from the primary extraction columns and equipment for calcination of the metal nitrates in the concentrated raffinate to produce metal oxides and a stream of oxides of nitrogen. Conventional bubble cap plate absorption towers are used to recover the oxides of nitrogen from the gas streams from the raffinate calcination, from the digestion of uranium concentrates, from the denitration of the uranyl nitrate hydrate, and from the nitric acid dissolution of impure massive metal uranium. A bubble cap plate fractional distillation column is used to concentrate the evaporator product stream and other dilute nitric acid streams. The nitric acid produced in the absorption and distillation towers is returned to the digestion area of the refinery for further use.

Production of Green Salt (UF_4): Green salt (uranium tetrafluoride) may be produced by reduction of orange oxide (uranium trioxide) to brown oxide (uranium dioxide) followed by hydrofluorination, as shown in Fig. 4. Complete reduction of the orange oxide to the brown oxide is essential for high conversions to the tetrafluoride. The reduction is accomplished with hydrogen produced by catalytic dissociation of ammonia, a convenient source of hydrogen of the high purity needed. Anhydrous hydrogen fluoride (HF) converts the brown oxide to green salt. The excess HF used to achieve high yields of UF_4 is recovered from the hydrofluorination reactor off-gas stream by fractional condensation as 70 pct HF (returned to the supplier) and as anhydrous HF (recycled to the process). A residue is removed from the noncondensible gas, neutralized in a scrubber, and ultimately discarded.

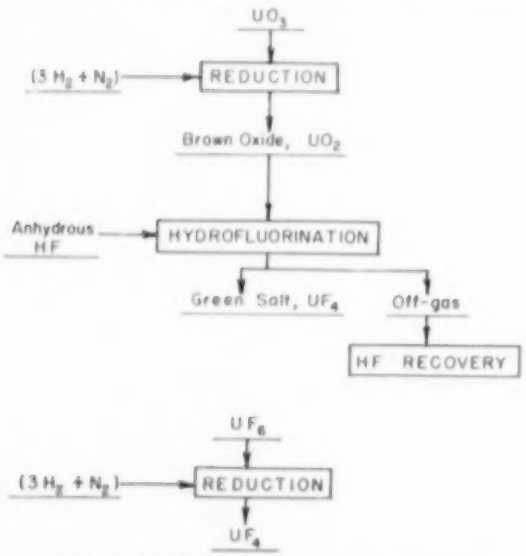


Fig. 4—Green Salt (UF_4) may be produced, either by reduction of UO_3 to UO_2 followed by hydrofluorination, or by the gas phase reduction of UF_6 with hydrogen.

Green salt may also be produced by the gas phase reduction of uranium hexafluoride (UF_6) with hydrogen. The use of dissociated ammonia is also applicable to this process, and the byproduct HF is recovered from the off-gas stream by condensation.

Reduction of Green Salt to Uranium Metal (Fig. 5): Green salt is mixed with metallic magnesium and charged into a dolomite refractory lined *bomb*. The bomb is capped and placed in a Rockwell furnace where it is heated until the thermite-type reaction between the tetrafluoride and the magnesium is initiated. With the high heat of reaction and the rapid rate of reaction, the contents of the bomb are melted and the uranium metal flows to the bottom of the charge cavity where it solidifies into a massive metal *derby*. After the bomb is cooled, the contents of the charge are removed, and the derby is separated from the slag, cleaned, weighed, and transferred to the melting and casting area. The slag is crushed and transported in portable hoppers to the metal recovery plant for recovery of uranium values.

Melting and Casting: The cleaned derbies are charged into refractory-lined crucibles, and the loaded crucibles are placed inside the induction coil of a vacuum induction furnace. After the metal is heated beyond melting temperature to superheat, it is ready for tapping. A special jig opens the tap hole, and the metal runs through the bottom of the crucible into the mold below. The metal is allowed to solidify in the mold under vacuum and is kept in the mold under inert atmosphere until the temperature has dropped to a few hundred degrees Fahrenheit. Then the furnace shell is opened, the mold is taken away and opened, and the ingot is lifted out by mechanical equipment.

The top of the ingot is cropped to remove pipe and impurities. A sample is cut off for chemical and physical tests, and the surface defects are ground off. Then the ingot is taken to the rolling mill.

Fabrication of Reactor Fuel Elements

The ingot is charged into an electrically heated salt-bath furnace, and in about one hour it reaches the required rolling temperature. The heated ingot is conveyed to a primary mill (Fig. 6) where it is rolled, with frequent turning on the sides, into a billet. The billet is run through a series of stands that reduce the cross section to a round, which is sheared to the desired length and either allowed to cool to room temperature or charged into a third salt-bath for heat treatment.

The round rods, either heat-treated or not, are straightened by rolling through a straightener, and the ends are sawed off so only sound metal remains. The rods, six at a time, are fed into Acme-Gridley screw machines, which machine the rods to the desired diameter, and cut the rods into slugs. They are fed through centerless grinding machines, where the diameter of the slug is reduced to the final size, and then the ends of the slugs are machined on lathes and the corners rounded. The finished slugs are pickled in nitric acid, washed, dried, and inspected for surface quality and soundness. After inspection, the good slugs are packed and shipped.

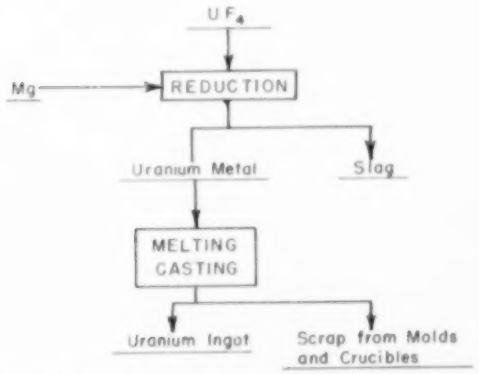


Fig. 5—Green salt is reduced to uranium metal by metallic magnesium in a dolomite lined bomb heated in a Rockwell furnace.

Recovery of Uranium From Reject and Scrap Materials

The bulk of the reject and scrap materials are produced in the metal reduction, casting, and fabrication areas. These materials may be grouped into two general types: 1) high grade metallic scrap, and 2) low grade and nonmetallic scrap. The metallic scrap consists of ends cut from the ingots and rods; sawdust, chips, and turnings from the machining area; and reject slugs. Where chemical purity permits, these are charged into the remelt crucibles with the virgin uranium derbies to produce ingots. When contaminated, they are processed in the metal recovery plant either by burning in a furnace to impure black oxide (U_3O_8) or by dissolving in nitric acid to form an impure aqueous solution of uranyl nitrate. In either case, the product is sent to the refinery as feed material.

The largest single source of low grade scrap is the slag fraction from the metal reduction step. Crucible and mold cleanings are burned and returned to the refinery as impure black oxide if they are of a sufficiently high assay; otherwise they are processed as low grade scrap. Uranium-bearing floor sweepings, dust collector residues, sump precipitates, etc. may also be included in this category. These materials are calcined in a furnace to oxidize residual free metal and burn organic constituents. The resulting furnace product is milled, acid-leached, and filtered to produce a uranium-barren filter cake and a uranyl salt solution filtrate. The uranium is precipitated as ammonium diuranate which is filtered on a precoat unit and converted to impure black oxide feed for the refinery by calcination of the cake in a direct-fired multiple-hearth furnace. A major consideration in the production in the metal recovery plant is the removal of chlorides and fluorides because of the increased corrosion these cause in the presence of nitric acid in the refinery.

Quality Control and Accountability

Throughout all the operations, extreme care is taken to maintain the identity of all products for process quality control and to provide the basis for an active and accurate inventory of all uranium on the site. All storage and transfers of uranium and uranium containing materials are accomplished in registered containers. The green salt is loaded into labelled cans, and the derbies made from the salt are numbered. The ingots are stamped with a number; the rods are stamped with a number identifying ingot number and rod position; and the slugs cut from the rods are numbered, identifying slug position, rod number and ingot. These numbers allow yield computation and tracing of the history of the slug back through the process chain.

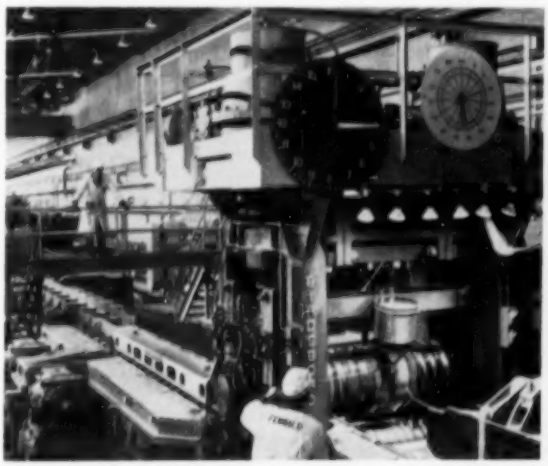


Fig. 6—This mill is used to roll uranium into rods for subsequent fabrication into reactor fuel elements.

Summary

An intricate series of process steps are required to produce uranium reactor fuel elements to meet the exacting product demands. A considerable amount of effort must be devoted to the recovery of excess reagents and of uranium from scrap and reject streams. Serious problems are encountered from the presence of corrosive reagents at elevated temperatures in two areas: the nitric acid recovery operation and the green salt reactors. These corrosion problems are met by careful construction and diligent process control. Although some new techniques are employed, basically the uranium production flowsheet consists of the application of a sequence of conventional industrial processes and operations.

Properties of Zircaloy-2

A recent zirconium alloy with improved corrosion resistance and strength for atomic reactor construction

by D. E. Thomas and F. Forscher

THE rapid development of reactor technology within the past five to ten years, with its needs for new materials, presents a challenge to the metallurgist, chemist, and materials engineer. Among the materials used in reactors is the new metal, zirconium, and its alloys, which are attractive from the point of view of their low neutron absorption. This desirable characteristic of zirconium is offset by its low strength properties and its highly variable corrosion behavior in the commercially pure condition. Zircaloy-2, a low alloy of zirconium, was developed by the Westinghouse Atomic Power Div. during 1952. Its desirable properties are: consistently good corrosion resistance in high temperature water, improved strength properties for design, sufficient ductility for fabrication, and little change in neutron absorption due to the alloy additions. Nominally, Zircaloy-2 is a sponge zirconium-base alloy containing 1.5 wt pct Sn, 0.12 wt pct Fe, 0.05 wt pct Ni, and 0.10 wt pct Cr. The use of Zircaloy-2 has increased in proportion to the development of water-cooled reactors. The purpose of this paper is to acquaint reactor technologists with concise and up to date information on the properties of this alloy. The information is subdivided into three sections: 1) composition and physical properties, 2) mechanical properties, and 3) corrosion behavior.

Composition and Physical Properties

Composition: A typical composition range according to specification PDS 11538-4 for Zircaloy-2 (strip, bar, or forging) is given in weight percent:

Tin	1.3 to 1.6
Iron	0.07 to 0.20
Chromium	0.05 to 0.16
Nickel	0.03 to 0.08
Average (Fe + Cr + Ni)	0.23 to 0.32
Nitrogen, maximum	0.008

The impurity content does not exceed the following limits in parts per million (ppm):

Aluminum	50	Magnesium	20
Boron	0.5	Manganese	50
Cadmium	0.5	Molybdenum	50
Carbon	500	Silicon	100
Cobalt	10	Titanium	50
Copper	50	Tungsten	50
Hafnium	200	Vanadium	50
Lead	100		

The limits on nitrogen content are included in the composition range because of its importance to corrosion resistance. No limit has been set on the hydrogen content, although its detrimental effect on ductility is known. The commonly encountered hydrogen content is about 40 to 50 ppm. The oxygen content varies between 1400 and 2500 ppm with a mean value of about 1800 ppm. The source of the oxygen is usually the sponge zirconium-base material which is always higher in oxygen than is crystal bar zirconium. The major contribution of the oxygen content is its strengthening effect at ambient temperatures, but this effect decreases with increasing temperatures.

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Physical Properties: The physical properties of Zircaloy-2 are listed as follows:[1]

Density:
6.55 g per cu cm = 0.237 lb per cu in.
(at room temperature).

Thermal expansivity:
6.5 (10)$^{-6}$ per °C
(from room temperature to 350°C).

Modulus of elasticity:
14.0 (10)^{6} psi ($dE/dT = -5500$ psi per °F).

Poisson's ratio:
0.31

Thermal Conductivity:

25°C	8.41 Btu per hr per ft per °F
100°C	8.12 Btu per hr per ft per °F
400°C	8.19 Btu per hr per ft per °F

Transformation Temperatures and Process Temperatures: Material initially in the hot rolled condition does not recrystallize completely in a time of 30 min until a temperature of 800° to 850°C is reached. Annealing in the α range for any reasonable time does not produce grain growth. The laboratory annealing treatment is 750°F for 20 hr in vacuum and furnace cool.

Dilatometer curves exhibit features due to a eutectoid reaction probably involving iron, nickel, and chromium, and due to the α-to-β transformation of zirconium as affected by the tin and oxygen content. On heating at a rate of 100°C per hr the reaction due to the presence of iron, nickel, and chromium begins at approximately 830°C, and transformation to β begins at about 900°C. On cooling the reverse reactions end at 780° and 870°C, respectively.

Mechanical Properties

The interpretation of most forming processes in terms of strength and ductility data obtained from tensile tests is, at best, a complex undertaking. Therefore, many other mechanical tests have been designed to simulate the expected forming operation or the expected service condition. For the purpose of this discussion, however, tensile strength and hardness on the one hand, and tensile ductility and impact data on the other hand, will be used to evaluate the effect of variables such as test temperature, heat treatment, cold work, and directionality on the strength and ductility of Zircaloy-2.

Tensile and Yield Strengths: The tensile strength in the longitudinal direction decreases with increas-

ing temperature as shown in Fig. 1. For comparison purposes the strength-temperature curve for arc-melted crystal bar zirconium is also shown. The square symbols represent the average of two tests in the as-received hot-rolled condition.[3] In order to evaluate the variability of the material, tensile specimens from ten ingots were tested and the standard deviation calculated.[4] The results are given in Table I, and the distribution at room temperature is sketched in Fig. 1. Tensile specimens taken transverse to the rolling direction differ little in strength from their longitudinal counterpart at all temperatures, but the data show a larger variability.

The effect of cold work on the strength properties is shown in Fig. 1 by the curve passing through the open circle symbols. The curve shows the increase in tensile strength at all temperatures caused by 60 pct cold rolling. This is close to the practical limit of cold working for Zircaloy-2, for further cold rolling produces pronounced edge cracking and often results in failure during rolling. It is perhaps surprising that strength properties in the longitudinal and transverse direction do not differ by more than a few thousand psi even after 60 pct cold rolling.

The yield strength (0.2 pct offset) of Zircaloy-2 parallels the behavior of the tensile strength with respect to the effects of temperature, annealing, and cold work. Typical values are shown in Table I.

Annealing decreases the strength properties at all temperatures as shown by the triangular symbols in Fig. 1. Annealing was done at 750°C for 20 hr in vacuum.

A typical metallurgical structure subsequent to the annealing treatment is shown in Figs. 2a and 2b. The stringerlike formation, which appears on longitudinal sections only, is also present in the as-received condition, and agglomerates to larger stringers at very high temperatures (1400°C).[4] The constitution of these stringers is, at present, not known. Stringers seem to have no major effect on strength properties, transverse or longitudinal to the rolling direction. The most pronounced effect of the stringers appears to be on shearability. The sheared surfaces are irregular when shearing is done in the direction of the stringers (i.e., rolling direction) and are smooth and even when sheared in the transverse direction.

Hardness: The hardness of Zircaloy-2 follows the behavior of the tensile strength. Diamond pyramid hardness values (Dph) at room temperature for the four curves in Fig. 1 are also tabulated on the figure and reflect, as expected, the strength level of the material tested. The values listed are based on a load of 30 kg. It should be remembered that even with a carefully prepared surface a very strong load dependence of Dph values is characteristic of zir-

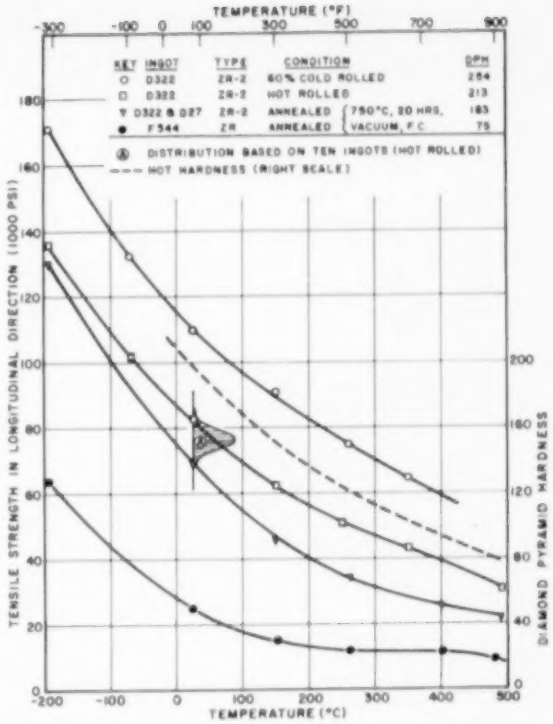
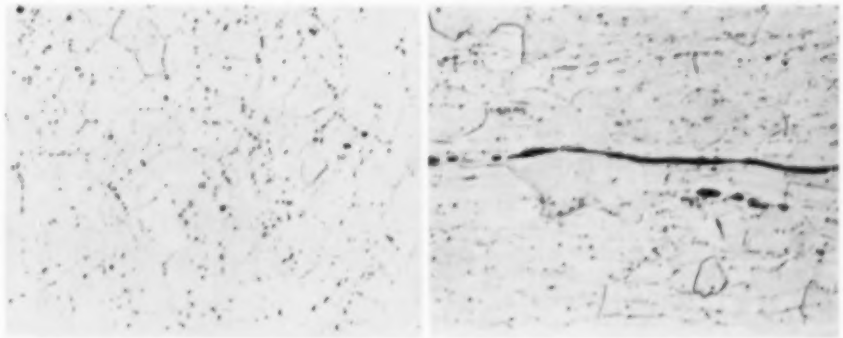


Fig. 1—Effect of temperature on the strength and hardness of Zircaloy-2.

Table I. Average Mechanical Properties of Zircaloy-2.*
One Specimen per Condition per Ingot from Ten Ingots

	Mean Value ± Standard Deviation			
	Room Temperature		260°C	
	Longitudinal	Transverse	Longitudinal	Transverse
	As-Received†			
0.2 pct yield strength, 1000 psi	49.4±5.5	70.0±4.8	24.4±2.5	34.1±6.5
Tensile strength, 1000 psi	75.6±3.2	77.5±5.1	41.5±2.2	41.8±5.0
Reduction in area, pct	28.3±5.2	37.1±6.3	42.2±8.2	52.4±3.8
	Base-Annealed‡			
0.2 pct yield strength, 1000 psi	44.5±1.8	67.8±2.3	—	—
Tensile strength, 1000 psi	74.8±1.7	74.0±1.6	—	—
Reduction in area, pct	28.4±2.6	40.0±3.4	—	—

The thermal history of as-received material is:
* 1) Forging at 980°C with an 80 pct reduction, 2) rolling at 845°C with a reduction of 97 pct, 3) 5 pct cold reduction, and 4) annealing at 845°C (1550°F) for 10 min.
† 750°C for 20 hr in vacuum and furnace cooled.



Figs. 2a (left) and 2b (right) —Structure of Zircaloy-2 subsequent to annealing is shown in traverse cross-section (2a) and longitudinal cross-section (2b). The stringerlike formation of unknown constitution appears to have no major effect on strength properties.

conium and its alloys.[5] This load dependence vanishes rapidly with increasing temperature; Dph values at room temperature become load independent only above 25 kg, and at liquid nitrogen temperature Dph values continue to decrease up to the limit of the load capacity of the hardness tester. Another consideration in hardness testing is its orientation dependence. The hardness on planes parallel to the rolling plane may be as much as 20 Dph units above the hardness on transverse or longitudinal cross sections. The latter impressions have a rhombohedral shape, and the ratio of the diagonals is a convenient measure of the anisotropy which exists perpendicular to the rolling plane.

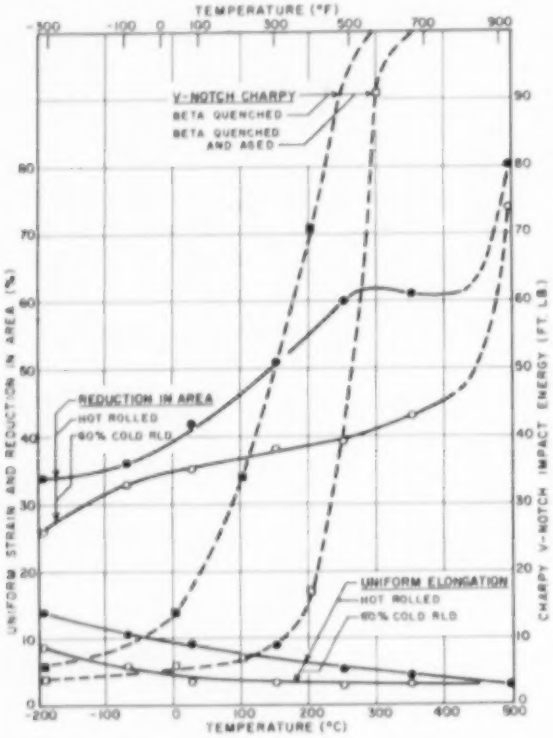


Fig. 3—Effect of temperature on ductility and impact strength of Zircaloy-2.

Hardness values as a function of temperature are shown by the dashed line in Fig. 1.[6] The parallel trend of tensile strength and hot hardness is apparent and may be expected to continue to such temperatures for which no experimental values of tensile strength are available. (The Battelle report[5] gives hot hardness data to 800°C). The logarithm of hardness (Dph) vs temperature plot is a sequence of two straight lines with a break at 550°C toward decreasing hardnesses.

Ductility: Ductility of any metal is a more elusive property than strength, and a plot of three measures of ductility as a function of testing temperature is shown in Fig. 3. The three measures are uniform elongation, reduction in area from tensile test data, and impact energy of *V*-notch charpy bars. Of the three sets of curves, the one for uniform elongation shows the smoothest variation with temperature. Uniform elongation is very nearly equal to the work hardening exponent n, because the natural strain (δ) at the maximum load (uniform strain) equals the work hardening exponent in a material which follows the power law $\sigma = K\delta^n$. This law is a good approximation of the plastic behavior of Zircaloy-2, i.e., when the true stress is plotted against the natural plastic strain on log-log paper, the stress-strain curve becomes nearly a straight line. Increasing temperature and cold work decrease uniform elongation as well as the work hardening exponent (Fig. 3). In the 60 pct cold-rolled condition the uniform elongation remains constant above room temperature.

The reduction in area is a complex measure of ductility, since it incorporates the uniform elongation as well as the heterogeneous (tri-axial) deformation beyond the point of instability, the so-called necking strain. Particularly in the latter stage the ductility is strongly influenced by microstructural discontinuities. From the curves in Fig. 3 it is apparent that the reduction in area is not a monotonously increasing function with temperature. Depending on the state of cold work, the increase in ductility with temperature is interrupted between 150° and 350°C. This behavior is reminiscent of the blue-brittle range in the low and medium carbon steels. The attenuation of ductility at these elevated temperatures is more pronounced in the transverse direction. Transverse specimens with more than 25 pct cold work exhibit a decrease of reduction in area with increasing temperature between 150° and 350°C. The ductility subsequently rises sharply at about 400°C. The reason for this deficiency in ductility at elevated temperatures is not known, although hydrogen is a suspected cause. The usual concentration of 40 to 50 ppm can be taken into solution at about 400°C which would explain the good ductility above this temperature, since hydrogen in solution is known to have no detrimental effect on ductility. On the other hand, it has been shown that in zirconium small amounts of hydrogen in the form of hydrides can greatly reduce the necking strain[4] and a similar effect is expected in Zircaloy-2. Fig. 4 shows a longitudinal section through the fractured end of a round tensile specimen containing 45 ppm of hydrogen tested at room temperature. Note the porosity which develops in the necked region presumably because of hydride precipitation and tri-axial strain. Also note the absence of a typical cup-cone failure of this

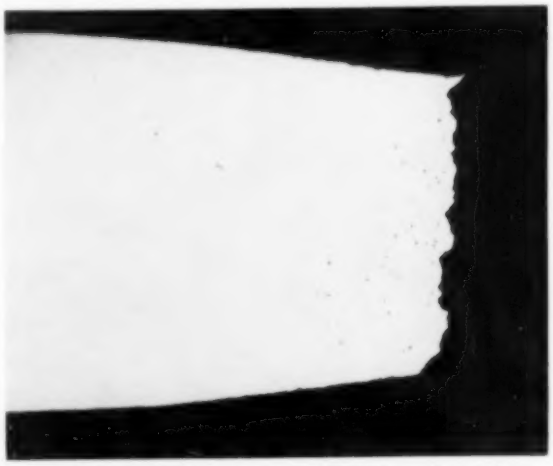


Fig. 4—Longitudinal section through the fractured end of a Zircaloy-2 tensile specimen containing 45 ppm hydrogen. Note porosity, presumably due to hydride precipitation.

ductile material. It is believed that the ductility of Zircaloy-2 can be increased by inhibiting the initiation of pores or, in other words, by preventing the precipitation of hydride. In this connection it is well to keep in mind the tendency of Zircaloy-2 to pick up hydrogen in corrosive media which is discussed in detail further on.

Another striking measure of the effectiveness of small amounts of hydrogen is its pronounced effect on the impact strength.[7, 8] The two impact energy curves show the typical transition temperature behavior of Zircaloy-2.[8] Let the 10-ft-lb level be an arbitrary definition of the transition temperature. It is seen that the β-quenched condition (1010°C for 1 hr in helium-water quenched) has a transition temperature of −50°C, while in the same condition an aging treatment (400°C for 3 hr and furnace cooled) increases the transition temperature by nearly 200°C. Mudge[7] has shown that this increase in transition temperature is associated with a metallographically observable formation of hydride. The hydrogen content pertaining to the impact curves in Fig. 3 is 40 ppm. Increasing the hydrogen content of Zircaloy-2 to 410 ppm shifts the transition temperature to nearly 300°C.[8]

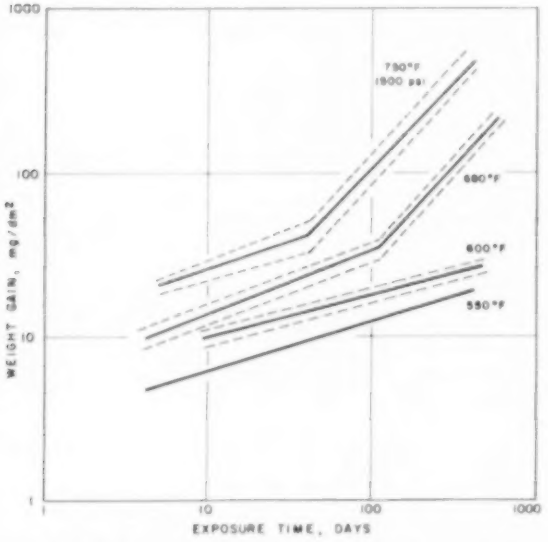


Fig. 5—Weight gain-time curves for Zircaloy-2 exposed to high temperature water and steam. The specimens exposed at 550°, 680°, and 750°F were previously annealed below 800°C. The specimens exposed at 600°F were exposed in the hot-rolled condition.

It would be an error to conclude from the results of impact tests alone that the β-quenched condition is beneficial with regard to ductility. Other effects will have to be considered, one of which is that β grain growth will occur when Zircaloy-2 is held in the β region (roughly above 1000°C). When these large grains are quenched into the α region the diffusionless transformation from body-centered-cubic β to close-packed-hexagonal α results in many α grains of related orientation within each parent β grain. The mechanical response of such a system is that the related α grains act as a unit as though the prior-β grain were present, and thus separation along prior-β grain boundaries during deformation is quite common. Whether this separation is due to impurity effects in the prior-β grain boundaries or due to differences in slip mechanism in adjacent prior-β grains (because of family relations among the α grains) is not known. The separation along prior β-grain boundaries has also been encountered upon welding in conjunction with shrinkage stresses.

Corrosion Properties

The most important single property of Zircaloy-2 is its excellent corrosion resistance in high temperature water in which respect it is vastly superior to unalloyed zirconium. The corrosion of unalloyed zirconium in high temperature water[9, 10] is characterized by the formation of a tightly adherent zirconium dioxide film during a more or less protracted period of exposure after which the oxide becomes nonadherent. During the first period a quasi-cubic rate law is followed, while in the second period a linear rate law is followed. The time at which the first period is interrupted is highly variable and is shortened when small amounts of nitrogen or other impurities are present in the metal. Further, the corrosion rate during the second period is very high. In the case of Zircaloy-2, however, the time at which the initial period is interrupted is highly reproducible and is relatively insensitive to impurity content. In the second period the corrosion product is adherent and the corrosion rate is low. These are the principal advantages of Zircaloy-2, and they become more pronounced with increasing temperature. A further advantage, which is derived from the decreased sensitivity to impurity content, is that Kroll process sponge zirconium can be utilized in Zircaloy-2.

Table II. Empirical Equations for the Corrosion Behavior of Zircaloy-2

Temperature °F	Temperature °C	Pressure, Psi	Equation: Δm in Mg per Dm²	t in days
550	288	750	$\log \Delta m = 0.50 + 0.30 \log t$	
600	316	1553	$\log \Delta m = 0.74 + 0.26 \log t$	Up to 1150 days
			$(\Delta m\text{-}34) = 0.065\ (t\text{-}1150)$	After 1150 days*
680	360	2705	$\log \Delta m = 0.76 + 0.38 \log t$	Up to 112 days
			$(\Delta m\text{-}34) = 0.37\ (t\text{-}112)$	After 112 days
750	400	1500	$\log \Delta m = 1.10 + 0.32 \log t$	Up to 41 days
			$(\Delta m\text{-}41) = 1.27\ (t\text{-}41)$	After 41 days

* Estimated.

Kinetics: The kinetics of the corrosion of Zircaloy-2 in high temperature water are shown in Fig. 5. Since the corrosion produced oxide remains on the surface, the increase in weight of the specimen is a measure of the amount of corrosion. Thus, in Fig. 5, the weight gain is plotted as a function of time on logarithmic scales for exposure in 550°, 600°, and 680°F water. During the initial period the corrosion kinetics may be represented by the empirical equation:

$$\Delta m = kt^n \qquad [1]$$

where Δm is the weight gain, t is the exposure time, and k and n are constants, dependent on temperatures. The change from the initial kinetics to the final kinetics has been termed transition. The post-transition corrosion kinetics are described by a simple linear equation relating weight gain and exposure time. A transition is not shown for exposures at 550° to 600°F, since data for long exposures are not available, although estimates may be made.[11] The kinetics data are summarized in Table II in which the logarithmic form of Eq. 1 is employed.

Included in Fig. 5 and Table II are data pertaining to the exposure of Zircaloy-2 to superheated steam at 750°F and 1500 psi. Under these conditions Zircaloy-2 appears to follow the same type of kinetics as it does in water at lower temperatures. This is further substantiated by the fact that curves relating corrosion to composition have the same features whether exposure is in steam or in water. Such a steam test has been employed extensively as an accelerated test, and frequent reference will be made to the results of such tests in this paper.

The Effect of Composition: The corrosion properties of Zircaloy-2 are not sufficiently sensitive to composition so that reasonable variations about the nominal composition need not be of concern in the practical sense. In the case of alloys containing iron or nickel, maximum corrosion resistance occurs at about 0.25 wt pct, while chromium appears to be less effective. Attempts to determine the individual effects of iron, nickel, and chromium in normal Zircaloy-2 have failed to show any marked dependence. However, the data suggest that corrosion resistance passes through a maximum as the combined iron, nickel and chromium content increases. This effect is suggested in Fig. 6 where the total range of combined alloying elements is somewhat greater than the specified range.

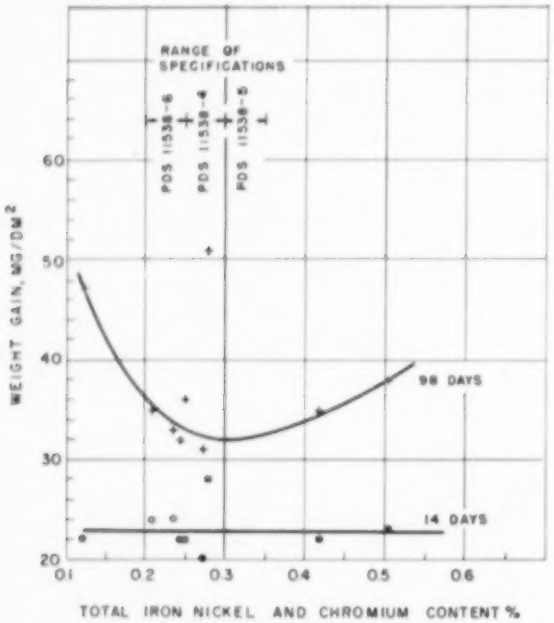


Fig. 6—The effect of total iron, nickel, and chromium content on the corrosion of Zircaloy-2 in water at 680°F.

On the basis of work done on Zircaloy-2 and other zirconium-base alloys the functions of the alloying elements may be discussed.[10] Tin in Zircaloy-2 overcomes the deleterious effect of impurities, which may be in the sponge feed stock, and promotes the adherence of the corrosion product. The reasons for the latter function are not understood. However, the action of tin in counteracting the harmful effect of nitrogen is believed to be due to the clustering of Sn^{+4} ions, N^{-3} ions, and vacant O^{-} sites in the oxide lattice. This tends to prevent O^{-} vacancies, formed as a result of the presence of N^{-3}, from participating in the transport of O^{-} through the oxide.

Iron, nickel, and chromium are believed to be interchangeable in their functions in Zircaloy-2, although chromium is less effective than the other two. These elements also tend to counteract the effect of nitrogen, possibly through a mechanism such as for tin. They also contribute to adherence of the oxide. Unlike tin or any other alloying elements, iron and nickel, and to a lesser extent chromium, improve the corrosion resistance of zirconium apart from effects involving impurity elements. This effect is believed to be associated with the corrosion product, hydrogen, which may play a role in corrosion failure. In the case of Zircaloy-2 it is believed that iron and nickel, and possibly chomium, promote the recombination of nascent hydrogen, produced at the surface by the corrosion reaction, and thus limit the amount of hydrogen picked up by the metal.

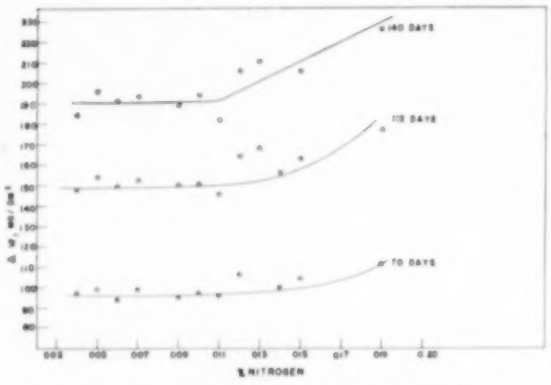


Fig. 7—The effect of nitrogen in Zircaloy-2 for varying exposure times in superheated steam at 750°F and 1500 psi.

The effect of nitrogen content upon the weight gain after various exposure times in 750°F steam is shown in Fig. 7. It will be noted that the deleterious effect of nitrogen becomes evident at lower nitrogen concentration as the exposure time increases. Thus, the amount of nitrogen which can be tolerated will depend upon the severity of the particular application.

The effect of oxygen upon the corrosion properties of Zircaloy-2 is absent or very small in the range 400 to 2000 ppm. The effect of other impurities such as aluminum, lead, silicon, copper, and manganese is harmful when these elements are present in quantities somewhat greater than those indicated previously.[10] However, precise data are not available.

Effect of Heat Treatment: The effect upon corrosion properties of annealing at various temperatures from 500° to 1000°C, followed by either quenching or furnace cooling, is shown in Fig. 8. It is to be noted that annealing at 900° or 1000°C results in somewhat higher corrosion rates in 680°F water or 750°F steam than is the case for annealing at lower temperatures. The corrosion properties are not particularly affected by cooling rate.

Hydrogen Pickup and Effect of Hydrogen Content: Experiments, in which the hydrogen content of thin foil specimens has been determined as a function of exposure time in hot water, show that hydrogen is picked up during corrosion.[10,13,14] The source of hydrogen is presumed to be that evolved by the metal-water reaction, since the amount of hydrogen picked up is proportional to the amount

of corrosion. Zircaloy-2 picks up about 10 to 20 pct of the hydrogen evolved in the corrosion reaction in 750°F steam and about 5 to 15 pct of that at 680°F. Unalloyed sponge was found to pick up about 30 pct of the corrosion product hydrogen. The addition of hydrogen to the test water (2000 cu cm per liter) results in the pickup of as much as 13 times that in degassed water with no effect upon the corrosion rate.

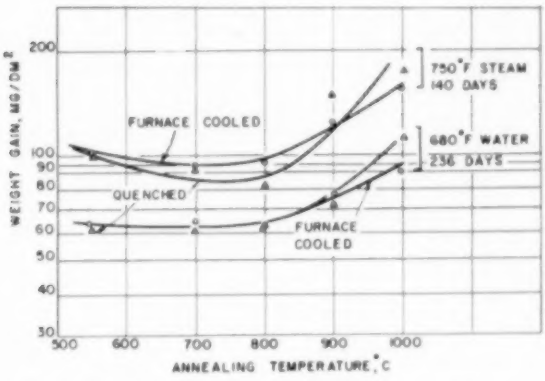


Fig. 8—The effect of heat treatment on corrosion resistance of Zircaloy-2.

Current incomplete data for specimens in which the initial hydrogen content varies from 4 to 10,000 ppm indicate that the corrosion rate increases gradually with increasing hydrogen content. The total weight gain of the specimens with 10,000 ppm H_2 after 42 days in 750°F steam is only about three times that for specimens containing 4 ppm.

The insensitivity of corrosion rates to hydrogen content suggest that hydrogen may not play an important role in the corrosion mechanism of Zircaloy-2. This is further substantiated by the fact that the kinetics of the oxidation of Zircaloy-2 exposed in pure, dry oxygen are identical to those of its corrosion in steam at the same temperature.[14]

Application of Corrosion Data: The limitation imposed upon the use of Zircaloy-2 by corrosion properties does not arise from consideration of the loss of metal and consequent mechanical failure. This is evidenced by the post-transition rates shown in Table II which range from 0.065 to 1.27 mg per dm^2 per day at 600° to 750°F. In terms of metal corroded, these rates correspond to 0.4 to 7×10^{-4} in. per year.

It is under conditions of heat flux through the surface that the corrosion properties of Zircaloy-2 become limiting in nuclear reactor application. In the case of a Zircaloy-2 clad fuel element there are three temperatures with which one is concerned. These are the surface temperature, the temperature at the metal-oxide interface, and the maximum temperature of the fuel material within the fuel element. Under conditions of constant heat flux and constant surface temperature, it is evident that the temperature at the metal-oxide interface increases as the oxide thickness increases due to corrosion, since zirconium dioxide has a very low thermal conductivity. The fact that the corrosion rate after transition is linear suggests that the reaction rate is limited by diffusion through a thin layer of oxide next to the metal and that the remainder of the oxide is relatively pervious. Thus, under heat throughput conditions the corrosion rate will increase as the oxide thickens. This effect is not pronounced until transition has been reached.

As corrosion proceeds and the oxide thickens under heat throughput conditions, the corrosion rate increases, and the maximum fuel temperature rises in a way which can be calculated.[15] The extent of corrosion is thus considered excessive when the fuel element cladding is breached or when the fuel temperature becomes too high. Which of these occurs first depends upon the particular geometry of the fuel element, the nature of the fuel material, the surface temperature, and the heat flux.

Conclusions

From this review of the mechanical and corrosion properties of Zircaloy-2 the following general conclusions are drawn:

1) Tensile strength, yield strength, and hardness decrease regularly with increasing temperature in the range from −200° to 500°C. Only small differences were found between longitudinal and transverse strength properties in the as-received and in the cold-rolled condition.

2) Ductility, as measured by uniform elongation, decreases regularly with temperature. Ductility, as measured by reduction in area, increases with temperature and reaches a plateau in the range from 150° to 350°C. With increased amounts of prior cold work, the reduction in area actually decreases with temperature in the range from 150° to 350°C.

3) Ductility, as indicated by impact energy, encounters a transition temperature at about −50°C. The transition temperature is raised by increasing hydrogen content or by heat treatments which precipitate hydride.

4) Zircaloy-2 corrodes in high temperature water at very low rates. Corrosion kinetics are initially quasi-cubic, and later become linear. The corrosion rate in the latter period is greater than at the end of the former period.

5) Nitrogen in excess of 60 to 100 ppm in the metal has a deleterious effect upon the corrosion properties of Zircaloy-2.

6) In general, metal attrition by corrosion is not a problem in itself. Rather the acceleration of corrosion, and the temperature rise within a fuel element accompanying the transfer of heat through the corrosion product, dictates the permissible corrosion rate or limits the useful lifetime.

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Inert Atmosphere Welding of Zirconium and Hafnium

by

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A. H. Kasberg, and R. B. Stermon

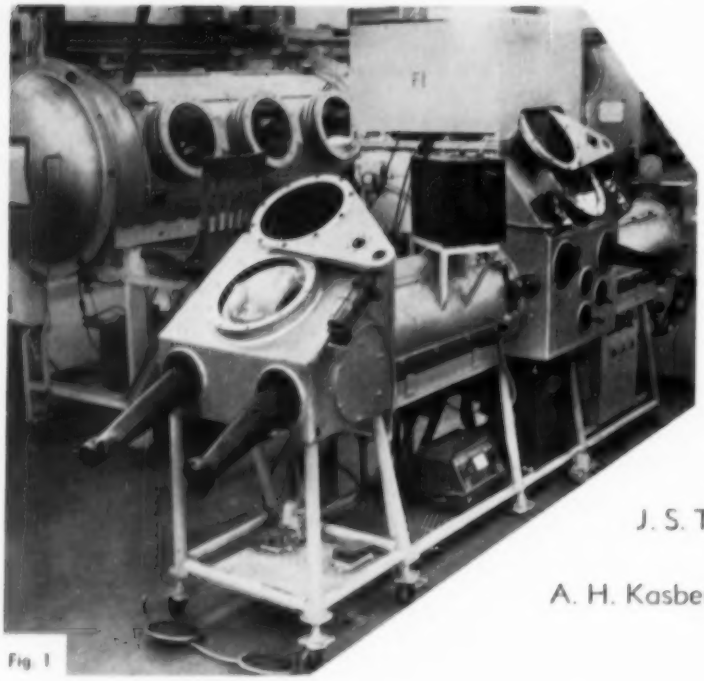

Fig. 1

ZIRCONIUM and hafnium are readily weldable to themselves and to each other when they are protected from atmospheric contamination. The low thermal expansivity of these metals and the very small volume change associated with the phase transformations permit the welding of complex structures with a minimum of distortion. These metals and their useful alloys are ductile over the entire temperature range, and the structures resulting from cooling through phase transformations are ductile, but the high chemical activity of these metals requires that an inert atmosphere be provided during welding. Failure to do so will result in the formation of nitrides, carbides, and oxides which are readily soluble in the metal and which impart brittleness to the weld area and reduce the corrosion resistance of the metal in high temperature and high pressure water. Ordinary inert, gas-shielded, tungsten electrode arc welding equipment is not adequate to prevent contamination to the degree desired for nuclear components. Consequently, special inert atmosphere welding chambers were designed and built. These have given excellent reactor proven results.

Early in the development of a zirconium welding technique, it was found that the most expedient method to obtain a good atmosphere was to evacuate the welding chamber first and then back fill with either pure helium or argon. Best results are obtained when the welding chamber is evacuated to less than 0.3μ prior to back filling. If the equipment has been in fairly constant use and is in good repair, satisfactory welds can be made with as little as 1 hr outgassing time. But it is imperative that all work and fixures entering the welding chamber be scrupulously clean and dry; otherwise the time for outgassing will be excessive. The inert atmosphere is usually maintained at or near zero gage pressure.

A typical welding chamber is shown in Fig. 1. The shell was fabricated from stainless steel in order to avoid contamination from surface of rust-coated metal. On such parts as access doors and observation windows, *O* ring seals are employed. All motions inside the welding chamber are initiated outside the welding chamber and transmitted to the inside through special rotary seals. Because of the difficulty of maintaining a good vacuum when using ordinary liquid lubricants, all bearings and sliding friction surfaces are operated dry. Some frictional relief is obtained through the use of dry molybdenum disulfide. Wherever possible, sliding bearing surfaces are eliminated in favor of ball bearings; excellent results have been obtained from ball bearings that have been thoroughly degreased, run in with dry molybdenum disulfide, and again degreased prior to installation.

The vacuum equipment is connected to the chamber near the center. All connections are kept as large in diameter and as short as possible. A very satisfactory combination of vacuum equipment includes a water-cooled baffle valve, a 700-cfm fractionating oil diffusion pump, an oil trap, and a 50-cfm mechanical fore pump. This system brings the 38-cu ft welding chamber from atmospheric pressure to 1μ in 1-hr and to 0.03μ in 2½ hr.

Relative motion of the work piece with respect to the electrode can be made independently in all directions. Longitudinal motion is imparted to the work holder, whereas the lateral and vertical motions are

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imparted to the electrode. The work piece can be rotated to permit welding on any side by means of hand operated controls. The welding current is supplied through a standard rectifier-type welder. The Heliweld unit provides an arc-starting device and automatically establishes the arc length through voltage control. No internal water cooling is provided for the electrodes, all cooling being accomplished through radiation and convection from finned electrode holders.

Thoriated tungsten electrodes are used for welding both zirconium and hafnium. Since water cooling is not provided, a larger electrode diameter than normal is selected to prevent overheating, but the tip is ground to a long gentle taper for best results. Under normal operating conditions, tungsten contamination is not encountered. However, if because of faulty operation, the electrode is brought into prolonged contact with the work, tungsten contamination will occur. The effect of tungsten contamination is to reduce the corrosion resistance of both zirconium and hafnium as well as to sharply increase the hardness. In the case of zirconium, the tungsten inclusions appear as local hard spots which seem to exhibit a particular vengeance toward cutting tools. The case of hafnium is quite similar except that the tungsten tends to diffuse over a larger area more readily. Contaminated areas in hafnium, containing less than 1 pct W, have been found to be very hard and friable at room temperature. The detection of tungsten inclusions in zirconium is quite readily accomplished by using X-ray techniques. However, since the X-ray densities of hafnium and tungsten are so similar, the X-ray detection of such inclusions is quite difficult.

The use of welding chambers limits the types of welded joints that are practical to achieve. For example, welding with filler wire is cumbersome. If the welding is to be accomplished by complete external remote control, synchronized wire feed devices would have to be employed. However, filler wire can be and is used when hand welding, but the operator must work through heavy rubber gloves, thus limiting his area of coverage. Furthermore, as welding progresses, the temperature of the inert atmosphere increases, causing an increase in internal pressure which tends to push the operator's arms out of the welding chamber.

Most zirconium and hafnium weld joints are designed so as not to require filler metal. If the atmosphere within the chamber is good, very little change is noted in the physical properties of the no-filler-wire welds, over those of the base metal. Only a negligible loss in ductility and increase in hardness is noted. Tensile tests made from flat welded specimens generally fail outside the weld area. There is a tendency for small gas bubbles to occur at the liquid-metal interface resulting from volatile impurities in sponge base alloys. However, this subfusion porosity does not appear to affect the physical properties of the welds.

Most of the no-filler-wire weld joints have been designed for 100 pct weld penetration. Depending on the accessibility, several methods of insuring this penetration are available. The easiest method is to weld from each side with conditions adjusted to give greater than 50 pct penetration. When both sides of the work cannot be welded, as in the seam welding of tubing, and if there is sufficient space behind the joint to place a close fitting copper back-up block, it is possible to cast the zirconium against the copper. There is little danger of contamination if the mass ratio of copper to zirconium is relatively high. If neither of the previous techniques is applicable, 100 pct weld penetration can be achieved through rigid control of the process. However, the proper welding process for each geometric configuration, basic alloy composition, and alloy melting procedure encountered must be derived experimentally.

Relative to most other commonly welded metals, zirconium and hafnium require high welding currents; approximately one ampere of current is required for every mil of penetration in zirconium. Hafnium current requirements are still higher. Those alloys melted under vacua require approximately 60 pct more current than those melted at atmospheric pressure. This effect is apparently due to the release of volatile impurities during welding, as is manifest by observation of the arc and weld puddle shape.

Zirconium to Hafnium Welding

Zirconium and hafnium can be readily joined to produce a ductile, corrosion-resistant joint. Because of differences in volumetric specific heat, thermal conductivity, and melting temperature, the weld pool shape is unique, Fig. 2. If the electrode is positioned over the joint, much more melting will take place in the zirconium, as is shown in Fig. 2a. This can be partly overcome by shifting the electrode slightly toward the hafnium to produce a weld similar to that shown in Fig. 2b. As is shown in these sketches there is a tendency for the molten metal to crowd up on the hafnium side of the joint, leaving an undercut on the zirconium side. If objectionable, this can be minimized by placing a small strip of zirconium, as is shown in Fig. 2c, which acts to fill the undercut. A complete weld will appear as shown in Fig. 2d.

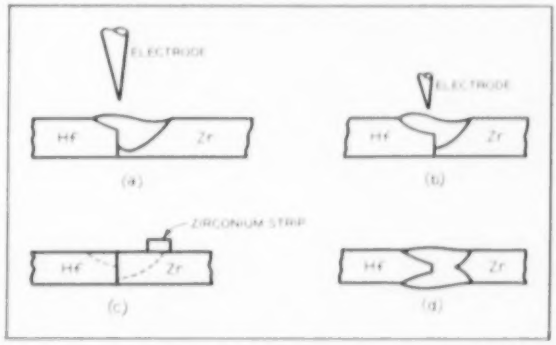

Fig. 2—The weld pool formed between zirconium and hafnium has a unique shape because of differences in volumetric specific heat, thermal conductivity, and melting temperature.

The physical properties of hafnium to Zircaloy-2 butt welds have been studied. At room temperature and up to about 200°F, the tensile fracture usually falls in the weld area. Above 200°F, the tensile failure is in the Zircaloy-2.

Resistance Welding

Some work has been done on resistance welding of zirconium alloys. Here, because of the short time at temperature and the chilling effect of both the work and electrodes, it is possible to produce corrosion-resistant welds with the use of a shielding stream of inert gas only. Comprehensive studies of resistance welds in zirconium alloys are being made at the present time, and it is expected that these results will be available in the near future.

First Zirconium Vessel for HRT Reactor

Fig. 1

Hot forming of complicated shapes reduced number of welds. Project speeded by development of equipment and techniques to permit welding in the open.

by G. E. Elder, E. C. Miller,
L. F. Bledsoe, and F. V. Daly

AT the Oak Ridge National Laboratory the nuclear stability of a liquid-fuel reactor has been proven by work in the Homogeneous Reactor Experiment.[1, 2] As a second phase of the program, the Laboratory will operate a liquid-fuel reactor of a more advanced design, designated HRT, or Homogeneous Reactor Test.[3] The core tank for this reactor is a spherical vessel with a conical section for the entry of the liquid fuel, as shown in Fig. 1.

Stringent demands are placed on structural materials and components in two-region power reactor systems. Core tank material must have: 1) low neutron absorption; 2) mechanical strength; 3) good corrosion resistance in reactor environments; and 4) resistance to mechanical damage by radiation.[4] These requirements severely limit the number of materials available for this application. The very low thermal-neutron cross section, the exceptional corrosion resistance in certain environments, and the retention of adequate strength at moderately high temperatures warranted selection of zirconium as the core tank's structural material. The contract for the development of the necessary procedures and the subsequent fabrication of the core vessel for the HRT was let to the Newport News Shipbuilding & Dry Dock Co. of Newport News, Va.

Zircaloy-2, specified for the core vessel, is a zirconium-base alloy containing: 1.5 to 1.65 pct Sn, 0.1 to 0.17 pct Fe, 0.07 to 0.14 pct Cr, 0.05 to 0.07 Ni, and a maximum of 0.009 pct N. Since this material had not previously been used in core vessel manufacture, investigation was essential to determine if and how the desired physical properties of strength and ductility could be attained in the forms required for this vessel.

The preliminary investigation program covered: 1) the selection of mill practices which could be used in reducing the ingot to plates and forgings having the requisite physical properties; 2) the evolution of techniques to form the component parts; and 3) the development of welding procedures to assemble the complete vessel.

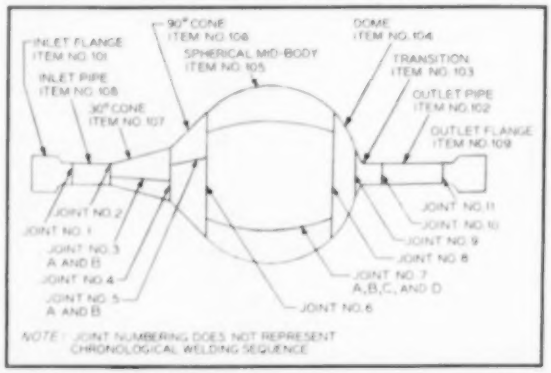
INLET FLANGE ITEM NO. 101
INLET PIPE ITEM NO. 108
30° CONE ITEM NO. 107
90° CONE ITEM NO. 106
SPHERICAL MID-BODY ITEM NO. 105
DOME ITEM NO. 104
TRANSITION ITEM NO. 103
OUTLET PIPE ITEM NO. 102
OUTLET FLANGE ITEM NO. 109
JOINT NO. 1
JOINT NO. 2
JOINT NO. 3 A AND B
JOINT NO. 4
JOINT NO. 5 A AND B
JOINT NO. 6
JOINT NO. 7 A, B, C, AND D
JOINT NO. 8
JOINT NO. 9
JOINT NO. 10
JOINT NO. 11
NOTE: JOINT NUMBERING DOES NOT REPRESENT CHRONOLOGICAL WELDING SEQUENCE

Fig. 2—The basic design of the vessel, with respect to the number and size of the various pieces, was first established.

The Crucible Steel Co., without prior experience with Zircaloy-2, produced satisfactory forgings and plates, employing a slight modification of mill practices based on procedures initially developed by the Westinghouse Atomic Power Div. and associated organizations.

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The basic design of the vessel (Fig. 2), with respect to the number and size of the various items of plate material, was established prior to any attempt to form the plate material, and experimental forming operations were carried out. Achievement of the necessary accuracy in the formed pieces was complicated by directional properties of the alloy.

It was anticipated that the problems associated with the welding of the alloy would be the most difficult to solve; therefore, every effort was directed to minimizing the number of welds required. Hot pressing was selected as the best method of producing the desired shapes, but in retrospect it appears that, had time permitted, spinning might have been a more satisfactory forming method. Machined forgings were employed for the inlet and outlet pipes and the outlet transition piece, but it is now evident that these components could have been fabricated from plate without undue difficulty and with a resultant saving in scrap losses.

Zirconium and zirconium-base alloys are extremely active chemically and require complete exclusion of the atmosphere by inert gas shielding to prevent contamination at welding temperatures. After consideration of all of the difficulties of welding in a dry box or a controlled atmosphere chamber, it was decided that efforts should be made to develop equipment and techniques that would permit all welding to be done in the open. A standard inert gas shielded tungsten arc torch fitted with an auxiliary trailing shield appeared so promising that the major effort was devoted to this style of equipment.

Fig. 3—Sections of the spherical mid-body were formed from 5/16 in. plate in this hydraulic press.

It was necessary to establish some criterion by which the efficacy of the inert gas blanketing by these devices could be assessed. Published reports indicated that the most applicable parameter was the hardness of the deposited weld metal and the adjacent heat-affected zones;[4] so, this property was selected as the measure of the efficiency of shielding.

Porosity in deposited weld metal presented some difficulty in a number of the test welds and in some welds made in the initial stages of fabrication. An increase in energy input and the adoption of helium, instead of argon, as the shielding gas materially reduced the porosity. All welds on the completed vessel were examined by radiography and ultrasonic methods and were sound, with a minimum of porosity.

Ingots

The ingots for the material were obtained through the Atomic Energy Commission. Blended sponge zirconium produced by the U. S. Bureau of Mines process, plus required amounts of pure tin, iron, chromium, and nickel, was double melted in a consumable electrode arc melting furnace under an inert gas atmosphere or in vacuum. The alloying element additions were made to the first melt and the arc cast ingots from this melt were used as consumable electrodes for the second melt. The second melt ingots were machined or ground so that no surface defects remained and internal soundness of ingots was assured by reflectoscope or a similar ultrasonic method of examination. No abrupt changes in diameter or local depressions that might impair subsequent fabrication were permitted.

Forgings and Plates

Items 101, 102, 103, 108, and 109 were machined directly from solid cylindrical forgings, except for the transition piece (103), which was reforged to provide greater length. Components 106 and 107

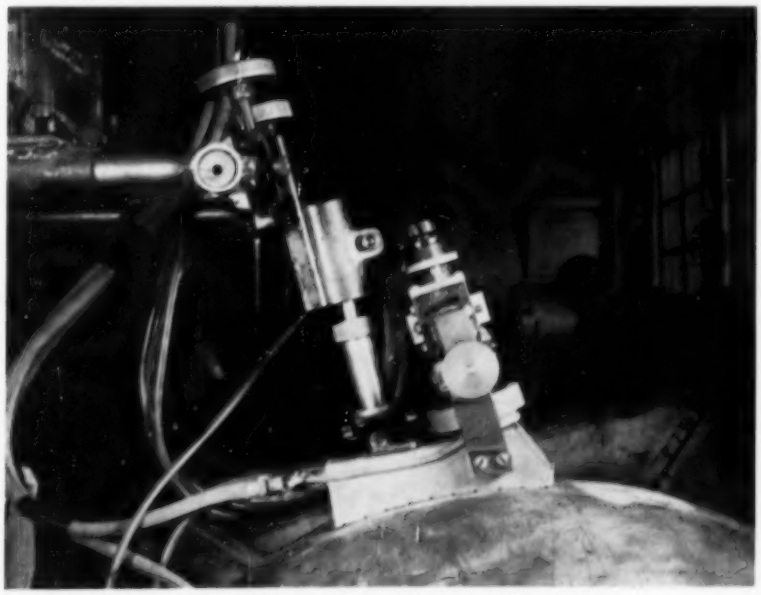

Fig. 4—Welding was performed in the open with a protective blanket of inert gas established under shields constructed to conform with each weldment geometry. Small notches at the contact edge of the shield permitted the flow of gas out of the area and prevented inspiration of the outside atmosphere. A hollow copper bar, conforming to the inner surface of the weldment, served as a backing shield.

were formed from ¾-in. plate, items 104 and 105 from 5/16-in. plate, and the diffuser screens were made from ⅛-in. material.

Forming

The 30° cone, the 90° cone, the spherical mid-body quarter sections, and the dome transition assembly were hot formed by using practically identical heating and forming cycles. The procedure employed was as follows: 1) the piece was heated in the furnace to a temperature of 1200° to 1225°F; 2) the piece was removed from the furnace and formed in partial dies until the temperature of the plate dropped to 750°F; 3) the plate was reheated to 1200 to 1225°F; 4) forming was continued until the plate temperature was 750°F; 5) the partially formed plate was reheated to 1200°F and held at temperature for 20 min; 6) full dies were used for the final forming operation, and the piece was held in the dies under pressure until the plate temperature was below 100°F. Fig. 3 shows the press and the dies used in forming sections of the spherical mid-body.

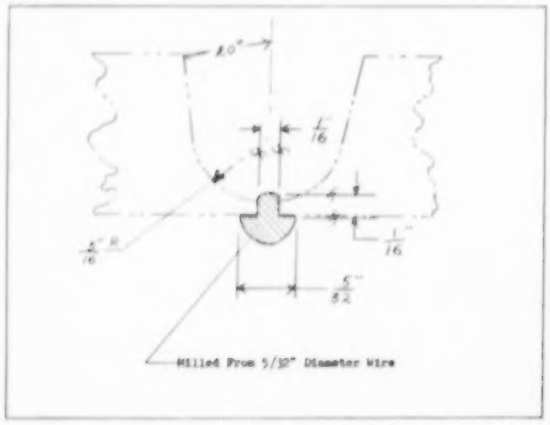

Fig. 5—A preplaced consumable insert was used in the root of all welds; it was tack welded to the root nose on one of the pieces. Wire for the second pass was 3/32 in. diam, and 1/8 in. diam wire was used for all subsequent passes.

Shielding and Welding

Weld fabrication of the vessel was performed in the open with a blanket of inert gas to protect the weld puddle, the heat affected zone, and completed weld above 1000°F. Individual shields conformed to each weldment, and inert gas was supplied at and behind the torch through holes in the center copper tube of the shield surrounding the torch, see Fig. 4. Small notches at the contact edge of the shield permitted gas flow out of the shielded area and prevented inspiration of outside atmosphere.

Except for some of the diffuser screens, welding was done in the downhand position. The external welding shield on which the welding torch and the tungsten electrode were mounted was spring loaded against the surface of the work. The joint being welded was moved under the shield and torch, using either a machine carriage for translatory motion or a welding positioner for rotary motion.

The filler wire used in the vessel fabrication was swaged Zircaloy-2 wire. The preplaced, consumable insert wire used in the root on all welds (Fig. 5), was machined from 5/32-in. diam wire by the Arcos Corp. Prior to fitup, the insert was tack welded to the root nose on one of the pieces. Before tacking the joint elements together, the area in the vicinity of the joint preparation was ground to remove all oxide film for about an inch from the machined edge. All ground and machined surfaces were stainless steel wire brushed to remove burrs, and these areas were then cleaned with acetone to remove any traces of grease or other contaminants. The joint elements were tacked together, without the addition of any filler wire, by fusing a small area of the top of the insert to each side of the joint.

The joint to be welded was extended by welding preformed Zircaloy-2 end tabs at the ends of each seam, as shown in Fig. 6. The end tabs were welded in an area of the assembly which was later removed by machining. Where possible, materials were sized to allow approximately 1/16 in. of extra width to provide for transverse shrinkage across each joint during welding. After tacking and welding of the tabs, the joints were again cleaned by brushing and by swabbing with acetone. Each welding joint was cooled between passes, and any oxide formed after passage of the shield on the preceding pass was completely removed by stainless steel wire brushing before making the next pass. Each pass was welded along the complete length of the joint in one continuous operation without pause. After the weld was completed, the weld reinforcement was removed by grinding, and the surfaces were sanded to a smooth contour.

Thus the first zirconium vessel for reactor applications was fabricated. The performance of this vessel in the Homogeneous Reactor Test at the Oak Ridge National Laboratory will contribute to the determination of the usefulness of this material for homogeneous reactor applications.

Fig. 6—The joint to be welded was extended by welding Zircaloy-2 tabs at the ends of each seam. They were later removed by machining.

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[4] Edward C. Miller: Zirconium and Nuclear Reactors. Zirconium and Zirconium Alloys, A Symposium Presented at the 8th Western Metal Congress and Exposition, ASM, Cleveland, Ohio, 1953.

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Fuel Element Design

by C. E. Weber

FUEL elements, the key to the development of nuclear power plants, are herein discussed from the point of view of a metallurgical engineer responsible for the design of a new or improved fuel element. He must make compromises between many factors either limiting the performance of the fuel element or the reactor in which it is to be charged. Fuel elements will be discussed as a generic class without extensive reference to a particular design, considering the interaction of factors which may limit performance.

Functional Requirements

Functionally, fuel elements must generally meet the following basic requirements:

1) Spatial fixation of the fissile material and the fission products.

2) Transfer of heat to the coolant at a desired temperature.

3) Isolation of fission products from the coolant.

4) Mechanical and dimensional stability.

If these conditions are met, the nuclear reactivity of the reactor can be kept constant, the fuel elements will not break or deform and interfere with coolant flow, nor will they get too hot with attendant problems. Isolation of fission products from the coolant will allow easy maintenance of the power generation system.

Upon choice of an endurance life, performance of specific elements can be evaluated against these requirements. A low reloading frequency is desired in most power-producing reactors to minimize reprocessing cost and fuel inventory. However, replacement of the fuel elements will ultimately be required, either to extract the fission products which act as nuclear poisons, or to replace the elements before extensive physical and mechanical damage occurs.

It is pertinent that the number of fuel element failures which can be tolerated is a function of the overall power plant design, being fixed by the amount of fission products and fissile material that can be tolerated in the primary coolant system. In comparing one type of fuel element against another, the fuel element quality may be defined as the product of the number of fuel element failures per core loading by the consequences of failure of an element. While this definition of quality is simple, one finds that comparisons have been made on the basis of one factor or the other when both should be considered.

The Anatomy of a Fuel Element

To provide a basis for subsequent discussion of design factors and radiation damage, the anatomy of a typical cylindrical, externally-cooled fuel element is illustrated in Fig. 1, taken from *The Metallurgy of Reactor Fuels* by Howe.[1]

During the fission event, the kinetic energy of the fission products is transferred to the lattice primarily through ionization, producing the typical temperature gradient shown. Concurrently, the moving fission products may hit and displace atoms from lattice positions, as described by Seitz and other authors,[2] causing damage to the lattice. The thermal gradient produced in the element will result in thermal stresses in the core and cladding as indicated. The fission products ultimately come to rest, that is, thermal equilibrium is established with the lattice atoms. The fission products exist as impurity atoms thereby causing damage, since, on the average, the fission product atoms are larger than the lattice atoms and metallurgically dissimilar, and hence may introduce local strains in the lattice. If the temperature, which is determined by the ambient coolant temperature and the gradient due to heat flow, is high enough, then diffusion of the fission products may occur with excessive swelling resulting from agglomeration of the rare gas atoms.

The rate of interaction between the coolant and the cladding is a function of the surface temperature of the element. This is fixed by the temperature drop across the stagnant boundary layer of the coolant chosen. The interface temperature between the core and cladding determines metallurgical or chemical reaction rates at this point.

Temperature and Specific Power Limitations

The specific power level and the fuel element temperature are two very important design factors which may effect the performance of the fuel element. Equally important is the fact that variations in these two design criteria directly affect the heat output of a reactor, the working temperature of the coolant, and thermodynamic efficiency of the cycle.

Although the temperature at any point in a fuel element is not independent of the specific power level which determines the thermal gradient in the element, the fuel element temperature and the specific power will be discussed separately. Temperature sensitive criteria may limit performance even at low power levels, while criteria sensitive to the specific power, such as thermal stresses, can, as a first approximation, be discussed as independent of the temperature of the fuel element.

Temperature Limitations: At any point in a fuel element, the rate of metallurgical or chemical change is determined by the temperature, while the physical and mechanical properties are determined by a temperature average over the element.

Referring to Fig. 1, the following variables are dependent on temperature:

1) Rate of interaction of the coolant with the cladding.

2) Rate of inter-diffusion of dissimilar cladding and core materials.

3) Rate of diffusion of fission products through the core and into the cladding material.

4) Rate of agglomeration of fission products and subsequent swelling.

5) Rate of chemical or metallurgical reaction between a dispersed phase in the core material.

6) Rate of reaction of the core media with the coolant on cladding failure.

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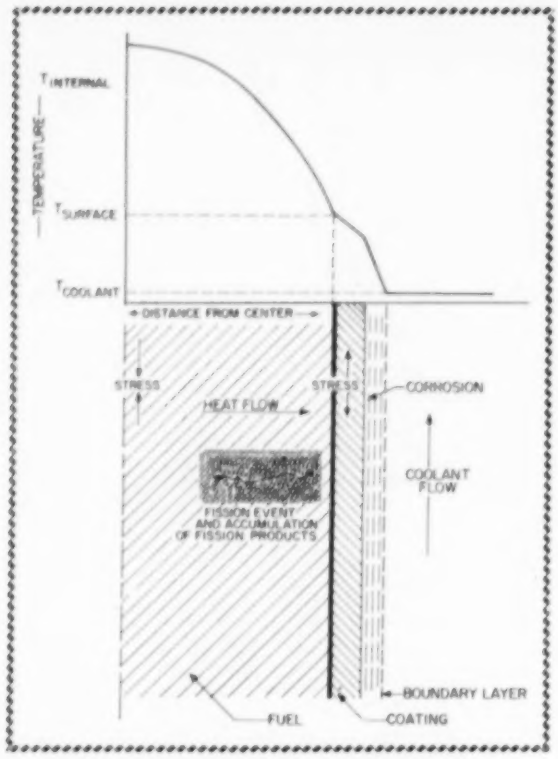


Fig. 1—Schematic diagram of fuel element heat flow.

7) Mechanical and physical properties of the composite element.

8) Crystallographic state of the core and cladding media—phase transformations.

Consideration of items 1 and 2, corrosion and inter-diffusion, leads to the choice of cladding material which must be compatible with the core material. For example, aluminum can be used in low temperature water, and does not react with uranium at room temperature. Zirconium can be used in contact with water up to the critical temperaure, 374°C, and does not react with uranium until even higher temperatures are reached. At higher temperatures, stainless steel is desirable for stability to many coolants, but its interaction with uranium to form a low melting eutectic at 725°C must be considered.

Item 3, the rate of diffusion of the fission products into the cladding, should be considered as to possible changes of properties and possible contamination of the coolant system through excessive corrosion. For example, if the concentration of uranium were to build up to the parts per million range in an aluminum cladding, at a high burnup significant amounts of fission product activity would be present.

Item 4, the rate of diffusion of the impurity atoms, agglomeration, and subsequent swelling, may limit the maximum operation of the fissile materials. As Howe[3] has pointed out, nucleation and growth of xenon and krypton gas pockets must be expected at some temperature and gas atom concentration. LeClaire[4] has established that, while rare gas atoms are insoluble in metals, they diffuse in a normal manner if generated in place, and Reynolds[4] has studied fission gas atom diffusion in uranium. The effect of impurity atoms on the behavior of fissile metals is discussed in more detail in a later section of this paper.

The potential importance of item 5, chemical interaction of the core materials, can be demonstrated by considering the UO_2-Al dispersion-type fuel element used in the Geneva Conference Reactor. The mixture UO_2-Al is thermodynamically unstable with respect to reduction of the uranium and oxidation of the aluminum. If UAl_4 and Al_2O_3 are formed, much of the previous ductile aluminum matrix atoms will have reacted to form brittle compounds with an accompanying decrease in mechanical properties and thermal conductivity. Obviously the element must be fabricated and operated at temperatures where the rate of reaction is negligible.

Item 6, rate of reaction between the core and coolant materials, was referred to during discussion of the quality of a fuel element. The chemical reactivity and rate of reaction of a core material, such as uranium, with a coolant, such as high temperature water, must be considered from the point of view of potential cladding failure during operation. Reaction may occur at a very rapid rate, possibly of semi-explosive violence, and cause damage to the surroundings. This might be the case for uranium at high burnup containing many micro cracks and voids of the type reported by Konobeevsky et al.[5] Reaction might also take place smoothly and continuously without notice, except for rapid contamination of the coolant, the piping, and system components, providing an accessibility-maintenance problem. High quality and operation at conservative design levels offer one solution to this question, while use of a chemically stable fuel-coolant combination offers another.

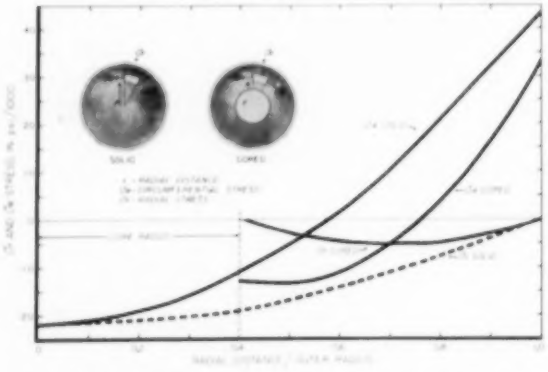


Fig. 2—Comparison of radial and circumferential stresses in solid and cored slugs.

Considering item 7, the mechanical and physical properties of a fuel element during operation are obviously determined by the average operating temperature of the element.

Item 8, phase transformations: the components of a fuel element may exist in more than one crystallographic phase in the design temperature range. For example, if uranium is used in power reactors, a high ambient coolant temperature such as 500°C may be required, while a desire for a large size and high specific power might lead to a high thermal gradient in the element, for example 300°C. If so, the metal would exist in three crystallographic states ranging from alpha phase in the outer lowest temperature zone to beta phase in the adjacent region and gamma phase in the high temperature zone. Severe distortion can occur under these conditions due to the large volume changes associated with

each transformation. These effects are brought about by the increment in stress level introduced in the metal by the expansion at the transformation point. This problem is discussed under Specific Power Limitations. Howe and Woolsey[6] have shown drastic experimental effects in the laboratory by heating and cooling uranium samples through phase transformations without radial temperature gradients.

Diffusion and agglomeration of fission products may be accelerated by phase transformations and recrystallization. LeClaire,[6] in studying the diffusion of argon in silver, has found that the diffusion rates are not constant. Burke[7] has pointed out that this may be due to easier accommodation of large fission product atoms at grain boundaries, resulting in their tendency to migrate with grain boundaries and to enhance the rate of motion over and beyond substitutional diffusion.

Specific Power Induced Stress Limitations: The specific power level in a fuel element will be limited by thermal stresses and stresses induced by phase transformations. Since other temperature sensitive reactions have been covered previously, the remaining effect of the thermal gradients introduced by heat flow are the stresses. Howe[1] has described the general case of the stresses in the cladding or core media limiting the specific power, giving general equations defining this parameter. He points out that plastic flow or relaxation may occur at high temperature, followed by brittle failure on cooling to a low temperature. Since most reactors do not operate at a steady state, excessive plastic deformation on both heating and cooling can also result in fatigue failure. The consequence of the stress introduced by the thermal gradients is considered in detail along with other stresses in the following section.

Stress Limitations: During operation, many types of steady state and cyclic stresses may be imposed on fuel elements. These are classified into two groups as follows:

Group 1—Externally Imposed Stresses:
- a) Vibration due to coolant flow.
- b) Stresses due to distortion of external reactor components.

Group 2—Internally Imposed Stresses:
- a) Thermal stresses.
- b) Phase transformation induced stresses.
- c) Circumferential stresses due to radial thermal gradients.
- d) Microstresses around fission product atoms or macrostresses around dispersed particles of fissile materials in a nonfissile matrix.

The externally imposed stresses are those commonly encountered from coolant flow and mechanical interaction of components. Their magnitude must be controlled and added to the internal stresses for a conservative design approach, based on knowledge of the mechanical properties of the fuel element components. Unfortunately, the mechanical properties of fissile materials containing design concentrations of fission products are not well known, and, as is shown in a later section, these mechanical properties can be drastically altered on irradiation.

The internal stresses introduced in a fuel element by thermal gradients and phase transformations can be large and hence are discussed separately. Circumferential stresses may result from uneven cooling or uneven power distribution in the elements and would act as an addition to the stress level. Microstresses or local stresses around the fuel particles in a matrix element present a different problem. For example, in a homogeneous fissile metal, microstresses may be introduced around fission product atoms which are large in size and do not fit in the lattice without considerable local microstrain. Such strains may effect the mechanical properties of fissile metals without introducing measurable strains. This problem is also discussed in a later section, under impurity atom effects.

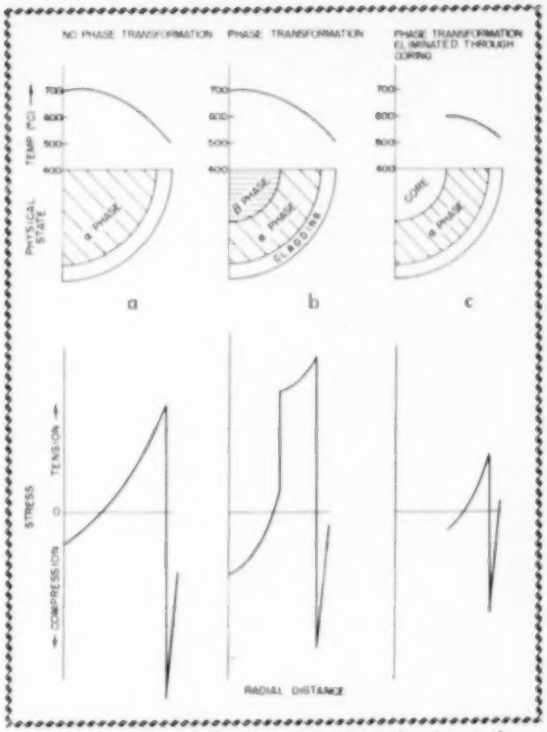


Fig. 3—The effect of phase transformation and coring on the calculated elastic stresses and temperatures for fuel elements of equal power.

Stresses Introduced by Thermal Gradients and Phase Transformations: Large stresses can be generated in fissile materials by these two mechanisms, leading to fracture of brittle materials and fatigue failure of ductile materials. Using the conventional tools of stress analysis, certain guiding principles and methods of reducing the stress level can be arrived at, even though the desired mechanical property data may not be available. The reader is referred to the literature for detailed information on techniques of stress analysis and, in particular, to the chapter in the *Reactor Handbook* on thermal stress analysis by Daane.[8]

For any given ductile metallic fuel element, as the power is increased, the stresses will increase until the elastic limit is exceeded. Plastic deformation can occur, partially relieving the stress under steady state conditions. On cooling, a reverse system of stresses is set up which, on continued cycling, can lead to fatigue failure. In nonductile materials, brittle fracture occurs if the elastic limit is exceeded.

For design purposes under conditions where cyclic stresses may be plastic, strains are calculated by assuming that elastic stresses may be compared with strain cycled fatigue data obtained experimentally. This approach also allows relative comparison of different elements of the same general type. On the

basis of a simple elastic model, the circumferential stress in a cylindrical element, S, is given by

$$S = \frac{E\,\alpha\,\Delta T}{4(1-\nu)}\left(\frac{3r^2}{a^2}-1\right) \qquad [1]$$

where E is the modulus of elasticity, α the coefficient of thermal expansion, ΔT the temperature difference in the element, ν is Poisson's ratio, while a is the radius of the element and r is the radial distance from the center to the point where the stress, S, is being calculated. Since in cylinders with internal heat generation, the maximum stress will be at the surface where fatigue failure is most likely to occur, the circumferential stress at the surface S' may be of greatest interest and is given by

$$S' = \frac{E\,\alpha\,\Delta T}{2(1-\nu)}. \qquad [2]$$

Further, a convenient relationship can be shown relating the maximum circumferential stress to the power generation per unit length Q and the thermal conductivity of the material K. Since

$$T = \frac{Q}{4\pi K} \qquad [3]$$

then

$$S' = \frac{E\,\alpha\,Q}{8\,K(1-\nu)}. \qquad [4]$$

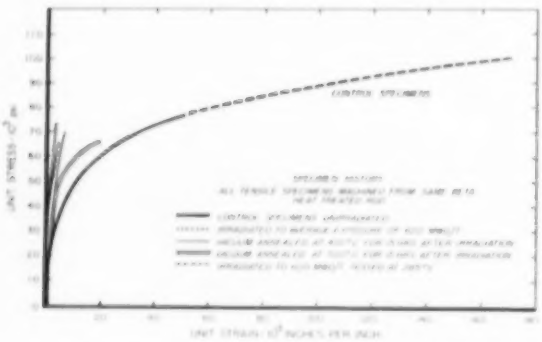


Fig. 4—Stress-strain curves of irradiated uranium at 285°C and at room temperature.

To illustrate the stress problem, a typical set of fuel element parameters set forth by Howe[1] is used, as given below:

Type of Element	Cylindrical
Type of Fuel	Uranium
Fuel Diameter	0.75 in.
Specific Power Level	415 watts per g U^{235}
Heat Flux	107 watts per sq cm (690 watts per sq in.)
Surface Temperature	538°C
Central Temperature	649°C
Thermal Gradient	111°C

The maximum circumferential stress, S' for this element, can be calculated using Eq. 4, taking the following for the approximate values of the physical constants of uranium at design temperatures: $E = 25\times10^6$ psi, $\nu = 0.25$, $\alpha = 18\times10^{-6}$ per °C, and $K = 0.75$ watts per in.-°C.

For a heat flux of 107 watts per sq cm, $Q = 1630$ watts per in., giving $S' = 163{,}000$ psi, which is well beyond the elastic limit of unirradiated uranium at these temperatures.

This elastic stress is, of course, fictitious, and plastic deformation would occur, presenting a potential fatigue problem, if the element is cycled many times from full power to low power. Since uranium may be embrittled by the fission products, the possibility of brittle fracture must also be considered.

Should the endurance life of the element be limited by fatigue failure, reduction of the stress level is one obvious solution. In most applications it is desirable to maintain the specific power level high, and the stress must therefore be reduced by geometry changes, increasing the surface to volume ratio or using more elements of smaller diameter. Since the nuclear value of the fuel in the central region of a fuel element may not be as great as in the outer volume due to self-shielding, a hollow core can reduce the stress level greatly without much loss of fuel. A comparison of radial and circumferential stress in solid and cored fuel elements is shown in Fig. 2, as presented by Cadwell and co-workers.[8]

The reduction in circumferential stress at the outer surface of the fissile metal is approximately 25 pct under the conditions chosen. Should the central region of uranium fuel in an element of this type exceed the α-β phase transformation temperature, a core would also provide space for the expanding metal to occupy, reducing the stress in the element. In this case, the β phase is about 1 pct less dense than α phase.

In a composite element with a dissimilar cladding, metallurgically bonded to a fissile metal core, the cladding may differ markedly in physical properties from the core, resulting in high stresses at the cladding-core interface. The effect of a phase transformation and coring on the calculated elastic stresses in the fissile and cladding material is shown in Fig. 3. The stresses are calculated for an element where the thermal conductivity of the core and cladding is the same, while the coefficient of expansion of the cladding is greater than that of the core. Condition a is the stress pattern in a solid element with a single phase core and a large difference at the cladding-core interface. With the central region expanding due to a phase transformation, case b, the cladding mismatch is the same but the circumferential stress in the outer fibers of the core is markedly increased. Coring as per case c and eliminating the second phase region compared to case b reduces the stress level throughout the element and such action should increase the fatigue life of the element.

Concluding the discussion on internal stresses, many solutions can probably be arrived at for minimizing these and other factors which may limit the life of a fuel element. Perhaps the unique difference in a fuel element relative to conventional items is the desire to obtain a large quantity of heat from nuclear elements, pushing the stress levels higher than in conventional practice coupled with the unusual effects produced by the fission products in the fissile material.

Bonding of Cladding to the Core: A general answer to the question of whether the core material should or must be metallurgically bonded to the cladding cannot be given. This is a pertinent question to be answered in each specific design case. For example, the uranium core is metallurgically bonded to the aluminum cladding in the fuel slugs for the Oak Ridge air-cooled research reactor. On the other hand, the cladding is only in tight contact with the uranium in the fuel elements for the Brookhaven research reactor as described by Gurinsky.[10]

Mechanical and Physical Properties of Fissile Materials

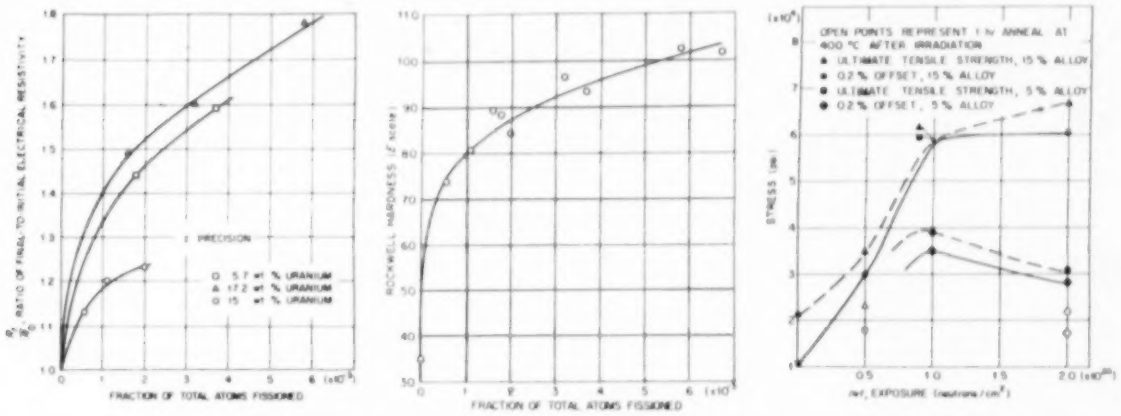
Stress considerations have shown that the thermal stress in a fuel element, for a given diameter and specific power, is proportional to the thermal conductivity and coefficient of thermal expansion. The resistance of fuel materials to deformation and failure is determined by mechanical properties. Conventional engineering design practices cannot be followed at the present time, due to the limited amount of data on mechanical and physical properties of fissile materials under design operating conditions. Significant changes take place in fissile materials under irradiation, but these changes can be incorporated into design only in a qualitative manner at present.

Current published data on the properties of irradiated fissile materials are given below:

Uranium

Ductility: Hueschen and Kemper[11] have found that uranium is embrittled on irradiation with a marked decrease in ductility, measured both at room temperature and at 285°C. Little recovery of ductility was obtained by annealing at 400° and 700°C. These data are shown in Fig. 4.

The irradiation dosage was 620 MWD/T, which corresponds to a lattice atom burnup of ~0.06 pct. Their inability to anneal out the damage at 400°C led them to the conclusion that the impurity fission product atoms must play a predominant role in the embrittlement.


RATIO OF FINAL TO INITIAL ELECTRICAL RESISTIVITY
PRECISION
5.7 wt % URANIUM
17.2 wt % URANIUM
15 wt % URANIUM
FRACTION OF TOTAL ATOMS FISSIONED
ROCKWELL HARDNESS (E scale)
FRACTION OF TOTAL ATOMS FISSIONED
OPEN POINTS REPRESENT 1 hr ANNEAL AT 400 °C AFTER IRRADIATION
ULTIMATE TENSILE STRENGTH, 15 % ALLOY
0.2 % OFFSET, 15 % ALLOY
ULTIMATE TENSILE STRENGTH, 5 % ALLOY
0.2 % OFFSET, 5 % ALLOY
STRESS (psi)
EXPOSURE (neutrons/cm²)

Effect of fission in aluminum-uranium alloys upon: the ratio of final-to-initial electrical resistivity (Fig. 5, at left); hardness (Fig. 6, center); and tensile strength at 30°C (Fig. 7, at right).

Table I. Effects of Irradiation on Properties of Uranium

Metal Condition	Micro-hardness, Kg per Sq Mm		Ultimate Tensile Strength, Kg per Sq Mm		Impact Strength, Kg per Sq Mm	
	Before	After	Before	After	Before	After
Cast (with increased carbon content)	327	416	35	21	2.1	0.6
Cast	333	413	45.2	13.4	2.92	0.76
Heat treated	368	440	55.3	28.4	2.2	0.71
Hot rolled	351	417	41.1	27	3.7	0.94

Radiation Exposure and Fuel Burnup Units. In this article, the fuel burnup is taken as the fraction of all the atoms, fissile and nonfissile, originally charged to the reactor. The resultant concentration of fission product atoms produced in the fissile material and damages that take place are directly related to the burnup. Neutron capture events have been ignored advisedly. In reporting fission product damage, units of exposure are frequently used rather than expressing data directly as the fraction of atoms fissioned. Two units of exposure most commonly used are MWD/T and nvt.

MWD/T is the measured total amount of heat produced in a unit of fissile material (a ton). Provided that all of the heat generated is measured, a conversion ratio of MWD/T to fission burnup can be calculated, assigning a value of the heat energy liberated per fission event. For uranium 1000 MWD/T = 0.13 pct burnup of all of the uranium atoms using 195 mev per fission.

The neutron dosage nvt is a much less exact measure of the burnup of a fissile material exposed in a reactor. The actual burnup can be calculated only if the experimenter also reports the correct average value of the fission cross section for the type of sample and the type of reactor used. In a thermal reactor the average value is a function of many variables, a few of which are average neutron temperature, neutron self-shielding in the sample, and local flux perturbation which can result in large cross section differences.

To provide a consistent basis of comparison for data quoted in this article, a value of 550 barns has been used, realizing that this is probably high, giving a conversion factor of 10^{19} nvt = 0.0039 pct burnup for natural uranium (10^{20} nvt = 0.55 pct burnup for 100 pct enriched uranium, and this value times the fraction of U^{235} present in uranium gives the total atom burnup in less enriched material).

It is proposed that a consistent fundamental unit of measure properly named be chosen by scientists and engineers working in the field of fuel element design and irradiation induced effects.

Reynolds[4] has shown that severe embrittlement of uranium can take place at as little as 0.001 pct of the lattice atoms fissioned in a uranium wire. Konobeevsky et al.[5] have also observed that uranium is brittle after irradiation with no elongation before failure in a tensile test. Their data on mechanical properties are shown in Table I, both before and after irradiation to an exposure of 10^{19} nvt. (Presuming the uranium to be natural, this corresponds to a burnup of 0.0039 pct.)

The decrease in ultimate tensile strength instead of the expected increase was attributed to many internal cracks which were detected microscopically.

Foote[12] states that the change in hardness on irradiation is large and depends on previous mechanical history. Alpha recrystallized specimens increased from Vhn 214 to 275 at 0.01 pct burnup.

Electrical Resistivity: Konobeevsky et al.[5] have measured the electrical resistivity of uranium fuels during and after irradiation to a dosage of 2.5×10^{19} nvt (corresponding to about 0.01 pct burnup for natural uranium). Resistivity increases from 1 to 5 pct were observed.

Billington[16] states that J. Royal (Argonne National Laboratory) has observed a 1 pct increase in resistance for 0.02 pct burnup of uranium lattice atoms.

Thermal Conductivity: No data on uranium are available, but a reasonable assumption is that the change in thermal conductivity will be proportional to the changes in electrical conductivity, since electron conduction predominates over lattice conduction in uranium metal.

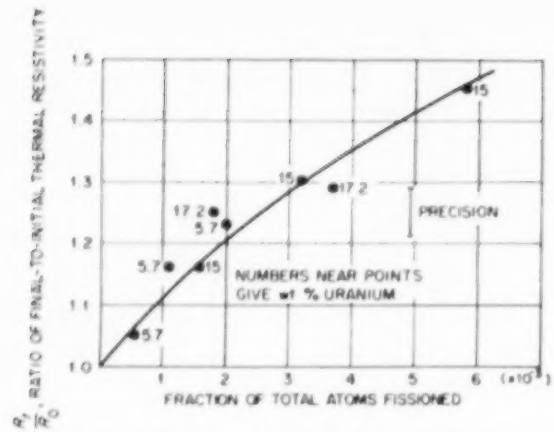

RATIO OF FINAL-TO-INITIAL THERMAL RESISTIVITY
FRACTION OF TOTAL ATOMS FISSIONED
PRECISION
NUMBERS NEAR POINTS GIVE wt % URANIUM

Fig. 8—Effect of fission on the ratio of final-to-initial thermal resistivity in aluminum-uranium alloys.

Uranium Alloys

Uranium-Aluminum: Data on property changes on uranium-aluminum alloys taken from Billington[18] are shown in Figs. 5 through 10. The enrichment of the uranium in these alloys is not given, and the burnup cannot be calculated. If natural uranium was used, lattice atom burnups of at least 0.078 pct were achieved at 2×10^{20} nvt. The tensile properties are markedly changed, and the material is much less ductile. Post-irradiation annealing gives only partial recovery, again indicating the role played by the impurity atoms.

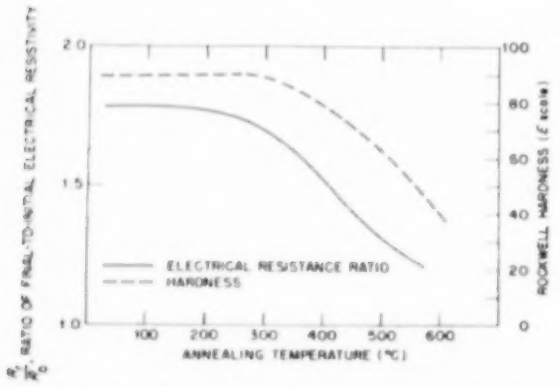


Fig. 9—The effect of annealing on radiation-produced changes in aluminum-uranium alloys.

Beryllium-Uranium and Zirconium-Uranium: Although Billington does not give extensive data, he states that these alloys are not much affected by irradiation. Electrical resistivity increases up to 9 pct were observed in the beryllium-uranium alloys at a total lattice atom burnup of 0.06 pct.

Fortunately, the change in electrical resistivity appears to saturate with increasing dosage. This may also be the case for the change in mechanical properties, but more data are needed in this field.

Ceramic Fuels: Uranium oxide and mixtures of uranium oxide in graphite and beryllium oxide have been studied.[15,19] Little data are reported on the uranium oxide, information being limited to X-ray line broadening at burnups as low as 3×10^{-4} pct of the uranium atoms.

Both the graphite and beryllia mixtures with urania show marked decreases in thermal conductivity. Changes of measurable orders of magnitude were reported for graphite-uranium oxide, while the conductivity was continuing to decrease in beryllia-urania after a sixfold decrease. In the beryllia case, the burnup was only 5×10^{-4} pct of the total atoms present.

The graphite-urania studies showed that no recovery of fission product damage could be achieved by annealing at temperatures up to 750°C. In addition, the studies showed that the amount of damage to the composite mixture was a function of the particle size of the UO_2 particles. Much less damage occurred for particles which were large compared to the fission product range, indicating that most of the damage was restricted to the UO_2. This dispersion approach is also discussed in a later section.

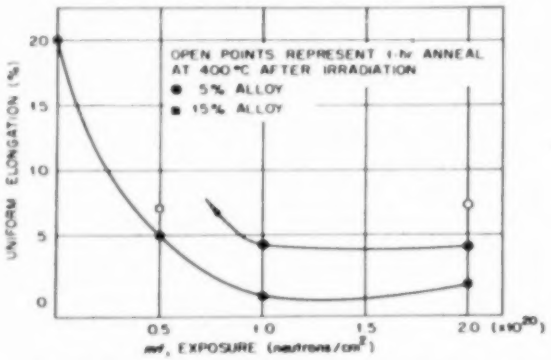


Fig. 10—Effect of fission on elongation at 30°C in aluminum-uranium alloys.

The data on mechanical and physical properties, including observations on dimensional stability, show that radiation damage, plus the generation of the impurity atoms in the lattice, can markedly change the properties of fissile materials. The need for additional data, including the temperature dependence, is obvious.

Radiation Damage and Impurity Atom Effects

In the discussion of *The Anatomy of a Fuel Element*, damage due to fast moving fission products displacing lattice atoms and the separate effect of the fission products at rest in the lattice was briefly mentioned. In this section, the difference between the two phenomena will be discussed in order to promote further work in this field.

The term *radiation damage* has been used, and in many cases is still used, to cover changes in mechanical and physical properties, dimensional instability, and other unpleasant effects that take place on irradiation of fissile materials. In this paper *radiation damage* will be limited to phenomena arising from the interaction of fast moving particles (neutrons and fission fragments) and photons (β and γ radiation). In a metal, radiation damage will occur only from the fast particles colliding with the nucleus of metal atoms, with heavy atom effects predominating over neutron effects. In nonmetallic systems, ionization effects may predominate, with β and γ radiation contributing significantly.

In contrast to radiation damage, the damage or change in properties caused by impurity atoms in the surrounding fissile lattice is an entirely separate phenomenon. While a whole new set of problems are created, the resultant material is not damaged by the foreign atoms. One may consider instead that a new material has been created with rather unique and perhaps unfavorable properties.

Radiation Damage: Determination of the relative contribution of radiation damage and impurity atom damage to altering the properties and behavior of fissile materials presents a new field for extensive and, what may prove to be, fruitful experimental investigation. In the absence of experimental results, data obtained on nonfissile materials can be extrapolated qualitatively to fissile materials. Billington,[13] Varley,[14] and Crawford and Wittels[15] have recently summarized data on nonfissile systems.

In nonfissile metals, increases in electrical resistivity, hardness, yield strength, and decreases in ductility, as well as other property changes, have been observed. These changes are due to displacement of lattice atoms from lattice sites by fast neutron bombardment. In a fissile metal the same general type of damage will occur with the yield of displaced atoms being greater from collisions of the fast fission products than from neutron collisions with the lattice atoms.

Fortunately, annealing and recovery of most of the radiation damage occurs with most metals of interest to the reactor designer at design temperatures. Billington[13] has pointed out the apparent relationship between activation energy for self-diffusion and stability of metals to radiation damage at different temperatures. This is related to the well known generalization that lattice atoms are equally mobile in all metals at temperatures which are the same fraction of the absolute melting points of the respective metals. For example, most of the radiation damage anneals out of aluminum well below room temperature in this low melting metal.

While most power reactors operate at high temperatures where annealing occurs by recombination of the displaced lattice atoms and the vacancies, a low temperature region may exist in fissile metals at which diffusion annealing does not occur rapidly, thereby allowing high concentrations of displaced atoms to build up in the metal lattice. For example, Bruch, McHugh, and Hockenbury[16] have shown that neutron bombardment raises the temperature for brittle ductile fracture in molybdenum above room temperature, and a fissile alloy having molybdenum, tungsten, or other very high melting alloys as the base metal may not be well behaved at temperatures where lower melting alloys may be satisfactory.

Cadwell and co-workers[17] have studied X-ray line broadening and line shift in uranium irradiated to very low exposures (of the order of 0.001 pct burnup) and have seen indications that most of the displaced atoms anneal on reaching room temperature.

Summarizing, radiation damage caused by lattice atom displacement does not play a significant role relative to impurity atom effects under most design conditions. More work to determine the contribution of radiation damage to the total damage in fissile metals is indicated and low temperature studies should be informative.

Impurity Atom Effects: A low temperature region was postulated in which high concentrations of displaced atoms and lattice vacancies might build up in a metal. Two other regions may be defined:

1) A middle temperature region where radiation damage anneals out during operation but diffusion of the fission product atoms does not occur.

2) A high temperature region wherein the impurity atoms are diffusing, permitting agglomeration or escape of the fission products.

The middle temperature zone represents the region of interest to the fuel element designer. Mechanical property data previously discussed have shown that the impurity atoms can markedly embrittle uranium and that annealing up to as high as 700°C does not permit recovery of ductility. This is not surprising if attention is focused on the metallurgical nature of the fission products and the size of these impurity atoms. The composition of fission products is as follows: 83 pct metals, 12 pct krypton and xenon. The composition of the metals only is: 42 pct $\leq$ the size of uranium, 21 pct large metallurgically incompatible alkali and alkaline earth metals, and 37 pct rare earths (comparable in size). With this in mind, if a hypothetical element of 100 pct U^{235} were irradiated to higher and higher fission product concentrations, a point would be reached at which the metal would be highly embrittled as observed experimentally. As even higher concentrations were attained, perhaps approaching 100 pct burnup, the metal might be so highly stressed that fragmentation might occur due to microstresses only.

It is also pertinent to point out that a volume expansion of the fissile metal should start to occur (if plastic deformation takes place) at some concentration of fission product atoms, since:

1) Two atoms are produced per atom fissioned.

2) The atoms are on the average larger than the parent fissile atoms.

Assuming metallic radii for the impurity atoms and ideal mixing, a swelling rate R, the percent expansion in volume per 1 pct fission of all the metallic atoms in the fissile metal, can be calculated. Since the average volume of the fission products is about two times that of uranium, $R \simeq 3$. This rate assumes no cracking or agglomeration of fission products, which would give a higher rate, or local elastic strain around the fission product atoms, which might reduce the swelling rate. At low burnups an expansion may not be detectable, but in high burnup elements such as MTR or perhaps elements of interest for certain types of power reactors this minimum amount of swelling may occur. Few data are available at present, but Billington[13] reports that Templeton, Brady, and Desnicke[18] have observed volume increases as great as 3 pct at 0.05 pct burnup of all the uranium plus aluminum atoms in an aluminum-uranium alloy. This gives a rate, $R = 60$, which strongly indicates other phenomena such as internal cracking or gas agglomeration must have occurred. Foote[19] states that changes in volume of irradiated uranium, about twice as great as can be accounted for by creation of fission products, have been observed in irradiated uranium, indicating internal cracking. Summarizing, until additional data are available, it may be wise to allow for a minimum volume increase due to fission product accumulation in the lattice.

Swelling and Agglomeration of Fission Products: At high temperatures the fission products are mobile and can diffuse and agglomerate in the metal or escape. Excessively high swelling rates may be expected if the fission gases, which are normally insoluble in metal agglomerate at grain boundaries, or

impurities exerting high internal pressure produce swelling through plastic deformation or cracking through brittle failure. Similar phenomena are known to occur in other metals, such as the case of hydrogen present in steel after quenching, leading to cracking and flaking.

LeClaire and Rowe[4] have shown that the rare gas atoms diffuse in metal in a normal manner. Reynolds[4] carried out an investigation of the diffusion of xenon and krypton in irradiated uranium at low concentrations ranging from 0.001 to 0.004 pct burnup and gas concentrations of 0.0044 to 0.018 cu cm per cu cm of metal, and found no appreciable gas evolution occurred below 1000°C on steady state heating. However, he noted that the rate of evolution at about 1000°C was considerably increased by cycling the metal down to low temperatures (well below the α-β phase transformation.) The acceleration is attributed to grain boundary motion, which results from cycling through the α-β and β-γ phase transformations. He also observed swelling and surface blistering of the uranium, due to gas evolution from the sample. At higher burnups in fissile metals even more pronounced effects might be expected.

Radiation Stability of Uranium: Alpha uranium appears to be the metal least stable to irradiation changes, and this instability has been attributed to the highly anisotropic nature of the metal in the α phase. Gross anisotropic distortion without a change in density has been observed both on irradiation and thermal cycling between two temperature gradients in the laboratory. This instability has been shown to be related to preferred orientation of the grains in uranium metal after fabrication.

Uranium has been studied extensively, and Foote[12] is referred to for a recent review with references to the literature. As an example of dimensional instability, he reports a sixfold increase in length on thermal cycling uranium with a highly preferred orientation. The metal also grows and distorts on irradiation, but randomly oriented, fine grain material is much more stable to both thermal cycling and irradiation. An example of dimensional changes as a function of preferred orientation is shown in Fig. 11, as prepared by Cadwell and co-workers.[17] On application an approach may be to contain the metal in a cladding strong enough to prevent distortion of the uranium. Since each grain in a randomly oriented crystal structure may still grow in a preferred direction, growth of grains into each other may set up a stress situation which accelerates microcracking of the type reported by Konobeevsky et al.[5]

While the behavior of uranium on irradiation and thermal cycling follows the same general pattern as a function of preferred orientation, the two mechanisms do not appear to be the same as recently reviewed by Pugh.[18]

To avoid the dimensional changes that occur in α-uranium and any effects therefrom, use of an isotropic material is indicated. Uranium stabilized in the γ phase meets this criteria, while thorium would be an isotropic matrix metal of interest in some power applications.

Fuel Types

The problem of radiation damage and impurity atom effects leading to embrittlement, dimensional instability, thermal stress-induced cracking, potential gas diffusion, agglomeration, and other changes has been discussed. Proper choice of temperature, power level, burnup, and fuel element shapes can solve many of the design problems. The type of material is also a design variable, and three general types of elements can be used.

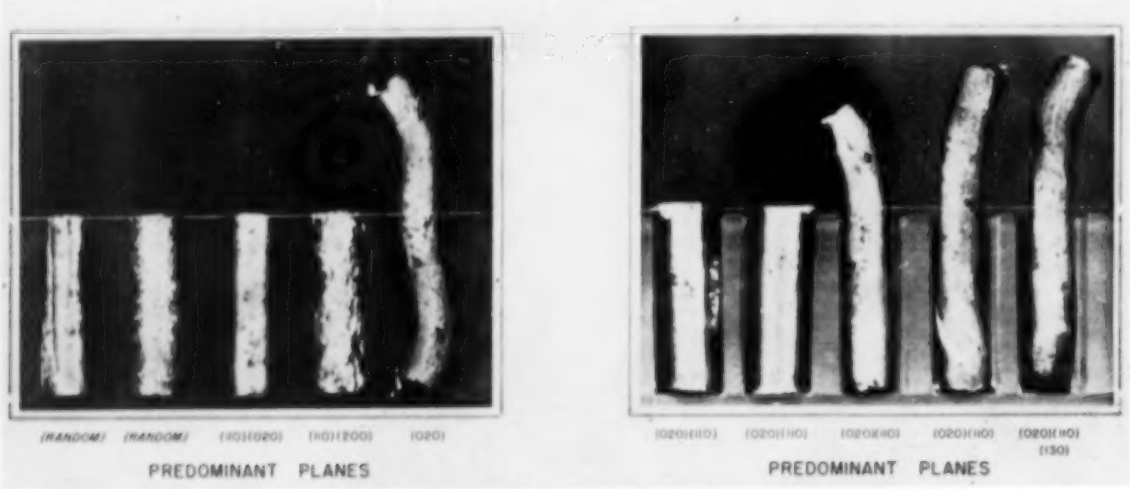


Fig. 11—Effects of preferred orientation on dimensional stability of uranium during irradiation. The horizontal white line indicates the original length of the specimens.

Type I. Elemental or Solid Solution Elements: Uranium, uranium alloys, and other fissile systems in which the concentration of fissile material and, therefore, the fission products produced are relatively uniformly dispersed throughout the fuel element core fall into one system. The system is characterized by the dilution approach in that the fissile material is diluted with an inert diluent, reducing the final concentration of fission products and the effects of operation on the endurance life. Uranium is a classic example of the fissionable material U^{235}, diluted with U^{238} as a nonfissionable base. The marked radiation effects in natural uranium where the burnup of all of the uranium atoms fall in the range of 0.01 to 0.1 pct has been discussed. This corresponds to a burnup of the U^{235} present of 1.39 to 13.9 pct of the U^{235} in the alloy of U^{235} plus U^{238}. Without dilution with U^{238}, these high burnups would

certainly cause marked changes in uranium stability. Other relatively low cross section metals such as molybdenum, zirconium, and aluminum can also be considered as diluents. Heterogeneous alloys, where all phases contain fissionable material, are classed as type I in contrast to the dispersion type, where the fissile material and the fission products are localized in a diluent matrix.

Type II. Dispersion-Type Fuel Elements: A dispersion-type fuel element has been defined by Weber and Hirsch[20] as an element in which the fuel core is heterogeneous, consisting of fissile particles dispersed in a continuous matrix of nonfissile diluent material. They point out the advantages of lumping

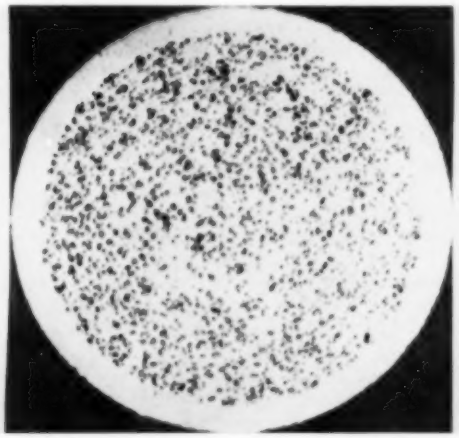


Fig. 12—This traverse cross section of an iron clad, Fe-UO_2 core, co-extruded from 2½ to ½ in. diam, is an example of a dispersion-type fuel element.

the fissile material into discrete particles of proper size so that most of the fission products are retained in the dispersed particle. The matrix metal must predominate in volume, being present as a continuous matrix. The particle size and spacing in the matrix is also chosen so that the distance between particles is large compared to the range of the fission products which recoil from the dispersed phase, leaving fission-product-free, matrix metal to provide the desired physical and mechanical properties.

An Fe-UO_2 dispersion is shown as an example of a dispersion-type fuel core material in Fig. 12. As reported by Billington,[13] L. P. Hunter and R. H. Kernohan both have studied uranium oxide dispersed in graphite and find that a suitable particle size is 100μ in line with the later analytical considerations of Weber and Hirsch.[20]

Type III. Container-Type Fuel Elements: Fig. 13 shows a third type of fuel element which was studied by Kesselring and Stahl at the Knolls Atomic Power Laboratory in connection with studies on a proposed intermediate neutron energy, power breeder reactor experiment. In contrast to dilution, the fissile material is placed in a container which in itself is not damaged by the fission events occurring in the fuel. The fuel is not bonded to the container walls, and tests on uranium and uranium oxide have shown satisfactory performances. In this case, internal void is provided in the container, allowing the fission gases to escape from the fuel, should this occur, without producing excessive pressure on the container walls.

The significant difference in this type of fuel element is that a large amount of damage could occur

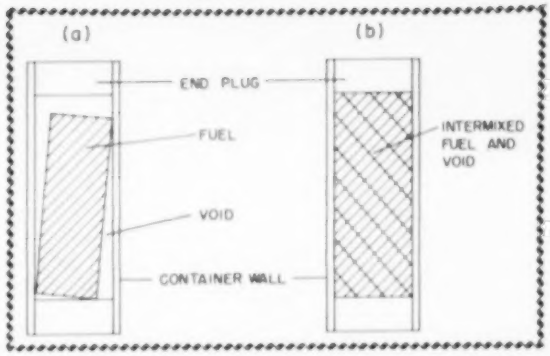


Fig. 13—This is an example of a container-type fuel element in which the fuel is not bonded to the container walls.

in the core while the container walls are not damaged by the impurity atoms produced.

Summary

Power plant design studies have well established that the cost of central station nuclear power is a direct function of the allowable fuel element burnup that can be achieved before reprocessing is required. Nuclear power can be competitive with conventional power if uranium fuel elements can be developed that will withstand exposures of 1 to 2 pct burnup of the fuel. The damage which takes place in an operating fuel element may well be the limiting factor in the cost of nuclear power. Basic fuel element design considerations have led to three general types of fuel elements for future study. Extensive investigations are required to determine the ultimate performance of these types of elements and their intrinsic behavior. Moreover, the advantages and disadvantages of a heterogeneous reactor compared to a homogeneous reactor can only be evaluated on the basis of this additional knowledge.

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Ceramic Fuel Materials for Nuclear Reactors

by J. R. Johnson

ONE of the major problems confronting reactor technology is the provision of suitable construction materials, particularly those in the reactor cores. The development of materials which can take advantage of the high power densities and high temperatures potentially available in nuclear reactors offers a special challenge. Ceramics have the possibility of meeting this challenge. In addition, there are reactor applications where ceramics are useful because of their inertness to corrosion and reaction, resistance to radiation damage, and economy.

Ceramics for fuel element use may be classified as fissionable and fertile materials either in bulk or granular form, and refractory container materials which incorporate the fissionable materials. In the selection of container materials, primary consideration must be given to nuclear economy, physical properties, availability, and fabrication costs.

A number of ceramics have been used in reactor applications, including graphite, a few oxides and carbides, and concrete. It is noteworthy, however, that little advantage has been taken of the refractory nature of ceramics, which is one of their most useful features. To some extent, the inherent complications of high temperature reactor systems have limited consideration and application of ceramics; however, the desirability of such systems provides justification for considerable research and development of these materials.

Definition and Properties

In general ceramics include those inorganic, nonmetallic materials which are processed or used at high temperatures. In bulk form they are brittle and usually hard, and nearly all are compounds of two or more elements. They include both solid and vitreous, or glassy, materials and may be part of mixtures with metals and organics, such as cermets and resin-bonded fiber glass. The elements, carbon, boron, and silicon are among those sometimes considered as ceramics, and the oxides, carbides, nitrides, borides, and silicides are usually classed as ceramic materials. The refractory hydrides, sulfides, and selenides, as well as some other high temperature compounds, have also been included. Table I lists some of these materials and their properties.

The densities given in Table I are theoretical. Some of the materials can be fabricated to very nearly theoretical densities, and most can be made at least 95 pct of those values. The melting points for the materials listed are not necessarily indicative of their usefulness at high temperatures. Some lose strength, become plastic, react with their environment, or are unstable at temperatures much lower than their melting points. A more characteristic value is the upper service temperature which depends on conditions of use.

The thermal conductivities of ceramics decrease with increasing temperature, often more so than metals. The conductivity of BeO, for example, changes by a factor of 10 between 20° and 1000°C. Changes by factors of two to five in this temperature range are not unusual. Nevertheless, many ceramics have higher thermal conductivities at 1000°C than alloys, such as stainless steels.

While the tensile strengths of ceramic materials are relatively low at lower temperatures, they are maintained in useful values at high temperatures. A number of ceramics, such as graphite, SiC, and some oxides, increase in strength with increasing temperatures. Because they are brittle, these materials fail in tension, with fractures originating at external or internal surfaces. Thus, they are sensitive to surface defects, flaws, and microstresses.

In ceramics there are often two or more kinds of atoms, each of which contributes to the structure and whose positions have identity. Slip in one direction may be possible, but this is not generally the case. Disturbance beyond the elastic limit does not result in yielding but rather in a rapidly propagated and usually complete fracture.

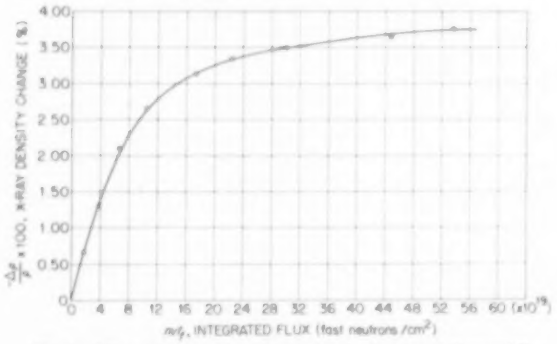

Fig. 1—Effect of neutron irradiation on the density of diamond.[1]

In metal structures, the systems often involve the closest packing of spheres so that cubic or hexagonal lattices are common. Ceramics, on the other hand, have structures scattered through all the possible systems, and they are often complex. MgO is face-centered-cubic, for example, while orthoclase feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) is monoclinic, and kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) is made up of alternate layers of pseudo-hexagonal octahedra and tetrahedra.

Although the atomic bonds are fundamental to the properties of ceramics, the finished ceramic material may be composed of grains which are sintered together or which are bonded with a glass or metal filling their interstices. In this case, interfacial ten-

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sions, degree of solid solubility, wettability, mechanical interlocking, and in general, surface phenomena, will influence or control many of the physical and chemical properties.

Of particular interest is the resistance of the brittle materials to thermal shock and cycling. In some reactor applications temperature changes may be rapid enough to impose severe thermal stresses, and it has been shown that repeated shock may eventually cause failure. Some cermets have been developed which are quite resistant to such treatment, but in general, the problem is best treated by proper design and engineering.

Engineering and Fabrication

Much of the practice in the fabrication and assembly of ceramic units and systems, large and small, is highly developed and compares favorably with the development of the engineering of metallic materials. The refractory linings of blast furnaces and glass melting tanks, the corrosion resistant glass

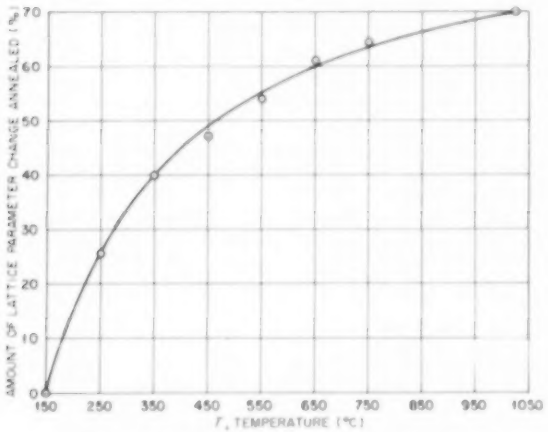

Fig. 2—Lattice expansion annealing in diamond.[31]

coatings on chemical reactors, and the complex glass plumbing systems in chemical plants are but a few examples of large units. Likewise, small intricate parts, such as bearings in fine instruments and insulators in electronic devices, are fabricated of ceramics. Many of these shapes must be made to extremely close dimensional tolerances.

On the other hand, with the possible exception of graphite, ceramics by themselves have not been developed suitable for very high temperature plumbing systems. Ceramic valves, elbows, tees, etc. made of pure oxides, carbides, and silicides may possibly be made, but they will not be available commercially in the foreseeable future.

Ceramics are formed by several techniques including pressing, extrusion, slip casting, hot pressing, and tamping. Except for hot pressed bodies, the formed ware is subsequently heated to obtain a strong dense products. Temperatures ranging from about 1000° to 2000°C are usually required. Machining to very close dimensional tolerances may follow, if required.

Radiation Effects

One of the requirements of ceramic materials for fuel element use is that they withstand nuclear particle bombardment under service conditions. While few data exist for ceramics subjected to fission fragment damage, there are numerous studies of neutron damage. In addition, there is some information on the ability of ceramics to retain fission products at high temperatures.

Temporary or permanent damage to reactor materials may occur as a result of fission fragments, fast and slow neutrons, and to a lesser extent, γ rays and β particles tunneling through crystal lattices at high velocity. Dislocations and excitations result, which affect the properties of the material. Disruption of lattices is accompanied by *healing*, which is dependent on diffusion rates, the compactness of the atomic structure, the nature of the crystal system, and the bonds involved. In general, it is expected that healing of ceramics at low temperatures would be much less than that of metals, but that at higher temperatures, where ceramics are useful, healing would occur readily. In fact, this has been observed, as well as a tendency for low temperature damage to *saturate* at some usually low level. Table II shows the effects of neutrons on a number of ceramics irradiated at temperatures less than 300°C, and Figs. 1 and 2 show the saturation effect and the healing that is possible.

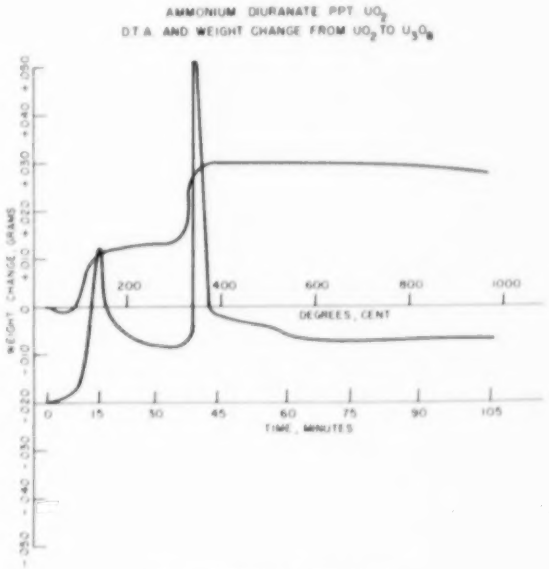

Fig. 3—Oxidation of UO_2 in Air

Some cubic latticies which are rather open, show very little, if any, dimensional changes even after severe radiation damage, although some weakening may occur as a result of local macroscopic damage coupled with gross thermal stresses.

Fission products generated in ceramic fuel elements[28] may diffuse out at high temperatures. It is expected that volatile isotopes, such as Xe, I, Te, Kr, and others, would diffuse readily, especially along grain boundaries at high temperatures. It has been found that dense, clad, sandwich-type ceramic elements, as well as stainless steel elements at high temperatures, retain approximately 99.99 pct of the volatile fission products generated, while unclad elements may retain only 90 to 99 pct in 24 hr tests.

Materials Selection

The selection of ceramic materials for fuel elements requires a careful evaluation of all requirements and an application of reasonable compromises.

The first criterion should be neutron economy. The materials must also have good high temperature strength, high thermal conductivity, good thermal shock resistance, and be nonporous. They should be resistant to radiation damage and be amenable to the chemical processing of spent fuel elements. Raw material costs and availability must next be considered. Finally, the materials must be readily fabricated into appropriate shapes.

Table III shows a list of ceramic materials, which have thermal microscopic absorption cross sections less than 0.5 barns, and includes fuel and fertile materials. These materials are potentially useful for high temperature reactor fuel elements.

In general, the oxides, with the exception of BeO, have relatively low thermal conductivities so that their use is somewhat limited to reactors of low power unless they are contained in another material. The carbides are difficult to form to maximum density; so, they are usually porous. Relatively little is known about the fabrication of silicides, although molybdenum disilicide has been studied at NACA.[28]

If neutron economy can be relaxed, there are several cermets which are possibly useful as fuel elements, including Cr-Al_2O_3, TiC-Ni, and ZrC-Fe. Of particular interest is SiC-Si, having a cross section of about 0.1 barns, a thermal conductivity higher than stainless steel at 1000°C, and other desirable physical properties. A very homogeneous nonporous body may be fabricated.

The compounds of uranium, including UO_2, are readily oxidized, requiring that they be heated only in inert atmospheres. Thorium compounds are usually less reactive in air, and ThO_2 is quite stable.

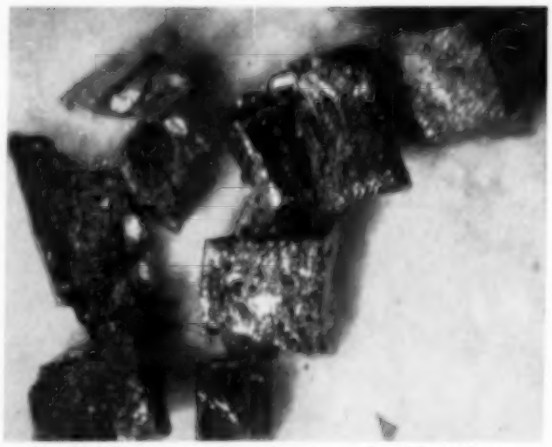

Fig. 4—UO_2 grains such as these are reduced by hydrogen from UO_2 hydrate crystals. They have the same external shape as UO_2, but are about 2/3 its size.

General observations of the properties of ceramics lead to the conclusion that for high temperature service, their use in gas cooled reactors shows most promise. Inert gases, which virtually eliminate corrosion problems, may be chosen. Closed cycle gas turbine power plants, which seem ideally suited for coupling to high temperature power reactors have been developed.

At high temperatures the diffusion rates of fission products through any material will be sufficiently high that some leakage from fuel elements will occur. By using only those materials which are ade-

Table I. Properties of Selected Ceramic Materials

Material	Melting Point, °C	Density,* G per Cu Cm	Thermal Nuclear Absorption Cross Section, Cm^2/Cm^3	Coefficient of Thermal Conductivity, G-Cal per Sec^{-1} $°C^{-1}Cm^{-2}Cm$
Alumina, Al_2O_3	2015±15[3]	3.79[15]	0.0101	0.069(100°C)[16] 0.021(600°C) 0.013(1200°C)
Beryllia, BeO	2530±30[3]	2.86[15]	0.00074	0.500(100°C)[16] 0.107(600°C) 0.039(1200°C)
Magnesia, MgO	2800[18]	3.58[20]		0.082(100°C)[16] 0.026(600°C)
Thoria, ThO_2	3220±50[18]	9.6[20]	0.0032 0.160	0.014(1200°C) 0.020(100°C)[16] 0.008(600°C) 0.0076(1200°C)
Urania, UO_2	2878±22[18]	10.02[20]	0.165	0.018(100°C)[16] 0.008(600°C) 0.006(1000°C)
Zirconia, stabilized 5 pct CaO, ZrO_2	2600[3]	5.32[15]	0.00571	0.004(100°C)[16] 0.004(600°C) 0.0049(1200°C)
Beryllium carbide, Be_2C	d. 2100[11]	2.44 *th.*[5]	0.0010	0.056(20°C)[5]
Silicon carbide, SiC	d. 2200[3]	3.2 *th.*[5]	0.00647	0.049(600°C),[12] (Recrystallized)
Uranium carbide, UC_2	2400[18]	11.28 *th.*[18]	0.192	0.082(20°C),[22] (10.0 g per cu cm density)
Zirconium carbide, ZrC	3530±25[3]	6.7[18]	0.0072	0.049(20°C)[1]
Molybdenum disilicide, $MoSi_2$	1870[1]	6.2[1]	0.0653	0.075(20° to 200°C)[13]
Uranium disilicide, USi_2	1700‡[18]	α-8.98 *th.*[1] β-9.25 *th.* α-high temperature 2.33 *th.*[27]	0.141	—
Silicon Graphite, C(g)	1430±20[27] 3700±100[7]	1.55[15]	0.00633 0.000350	0.20(20°C)[27] 0.298(100°C)[15] 0.154(600°C) 0.105(1000°C)
28 pct Al_2O_3-72 pct Cr SiC-Si	1300†[24] 1400†[30]	5.95[24] 3.1[30]	0.147 0.00659	0.04(20°C)[24] 0.5(50°C)[30] 0.06(1000°C)
TiC-Ni	1200†[14]	5.8[14]	0.311	0.080(20°C)[14]

* Bulk Density except as noted; *th.* for theoretical. † Maximum long time service temperature
‡ Calculated. § Burns in air at 800°C.

quately dense to retain most of them, and by providing traps in the power system, the activity of the machinery may be kept to tolerable levels. On the other hand, if by suitable design and proper shielding the circulation of fission products through the system can be accepted, as is the case in the circulating liquid fuel reactors, then many other materials may be considered for fuel elements. Graphite containing UO_2 is an outstanding example.

Bulk and Matrix Fuel and Fertile Elements

Only a few ceramic fuel elements have been made and given preliminary tests. Of these UO_2 and ThO_2 are examples of bulk forms, UO_2 of granular forms, and Cr-Al_2O_3 an example of ceramic matrix type elements.

UO_2—Rods of UO_2 have been made by isostatic pressing, then sintered in hydrogen at 1700°C, and machined to final dimensions. Not only is UO_2 quite refractory, but also it is resistant to corrosion by water up to several hundred degrees centigrade. Unlike the metal, it is safe to use in high pressure water reactors. Normally it would be metal jacketed, because of loss of fission products from its surface, and in high power reactors it would probably crack as a result of thermal stresses.

The rods have densities above 95 pct of theoretical. In order to obtain high density UO_2, there must be careful control of the starting material, forming method, and sintering. In general, high density UO_2 and ThO_2 may be obtained by: 1) use of very fine grain (submicron) starting materials, 2) use of additives or atmosphere control which accelerate sintering through defect structures and surface modification, and 3) use of dense (preferably fused) grains selected in particle sizes which will pack to maximum density. All of these techniques are followed by sintering. Dense UO_2 rods, plates, and bars have been made by each of these methods, but a combination of 1 and 2 is probably most effective and most economical.

The effect of oxidation in air and the need for careful atmospheric control are shown in Fig. 3. A fine grained UO_2 is first oxidized to U_3O_8 and then to U_3O_8. It may be noted that U_3O_8 is not stoichiometric above 500°C, as it loses oxygen gradually to about 1100°C and then rapidly changes back to UO_2 between 1100° and 1300°C. The changes $UO_2 \rightarrow U_3O_8 \rightarrow UO_2$ are accompanied by density changes 11 → 8.4 → 11 which, if not avoided, will disrupt the specimen.

Fuel element shapes of UO_2 may be made in many forms and dimensions. A practical upper limit for length is about 12 in. and thickness about 3 in. A lower dimensional limit would be a few mils for small (½ in.) disks or plates and 10 to 20 mils for rods.

ThO_2—Large ThO_2 rods can be made by a method similar to that used for UO_2 rods except that sintering is accomplished in air at about 1800°C. The use of ThO_2 as a fertile material shows considerable promise. It is also unreactive to high temperative water. As in the case of UO_2, its thermal conductivity is low, and with its

Table I. (Cont)

Linear Coefficient of Thermal Expansion, x 10^6, °C	Young's Modulus of Elasticity, x 10^6 Psi	Specific Heat, Cal per G, °C
6(20°C)[33]	52(20°C)[33]	0.21(20°C)[33]
7(500°C)	50(800°C)	0.25(500°C)
9(1000°C)	32(1400°C)	0.28(1000°C)
8(100°C)[33]	45(20°C)[33]	0.24(20°C)[33]
8(500°C)	28(800°C)	0.50(500°C)
9(1000°C)	12(1400°C)	
11(100°C)[33]		0.23(20°C)[33]
13(500°C)	12(20°C)[33]	0.26(500°C)
15(1000°C)		0.28(1000°C)
8(100°C)[33]	21(20°C)[33]	0.058(50°C)[11]
9(500°C)	18(800°C)	
9(1000°C)	14(1400°C)	
11.2(27° to 1260°C)[4]	25(20°C)[20]	0.056(17°C)[20]
7.2(70° to 1000°C)[9]	36(20°C)[9]	0.12(20°C)[33] 0.16(500°C)
10.8(38° to 982°C)[4]	45(20°C),[4] 6 to 8 pct porosity	—
4.7(20° to 1500°C)[5]	—	0.143(0°C)[37]
—	—	0.035(100°C)[130]
6.73(24° to 500°C)[20]	49(20°C),[19] hot-pressed	—
—	—	—
—	—	—
5(20°C)[37]	16(20°C)[37]	0.162(20°C)[37]
3.34(25° to 1800°C)[8]	1.0(20°C)[35]	ca. 0.03(20°C)[35]
5.85(25° to 800°C)[34]	47.2(25°C)[34]	—
4.2(20°C)[20]	35.8(20°C)[20]	0.228(400°C)[20] 0.252(700°C) 0.267(1000°C)
5.0(25° to 1000°C)[14]	56.7(1000°C)[14]	—

Table II. Radiation Damage to Ceramics by Neutrons*

Material		X-Ray Diffraction Pattern	Thermal Conductivity, K per K_0
Al_2O_3, single crystal	*A*	No change	—
	B	No change	1
Al_2O_3-3.5 MgO	*A*	No change	—
	B	No change	0.2
SiO_2 (vitreous)	*A*	No change	—
	B	Dimunition in halo intensity	1
ZrO_2 (CaO) (Stabilized)	*A*	Diminution in monoclinic phase	—
	B	Monoclinic disappears, cubic remains	0.75
ZrO_2-SiO_2	*A*	1.9 pct expansion, large loss of crystallinity	—
	B	No lines remain, crystallinity destroyed	0.2
SiC (α)	*A*	Line broadening 0.3 pct expansion	—
	B	Expansion and loss of crystallinity	—
BeO	*A*	Very slight expansion of c_0	—
	B	0.3 pct expansion c_0, none for a_0	1
TiO_2	*A*	No change	0.6
	B	No change	0.55
MgO	*A*	No change	—
	B	Crystal broken up $MgO + MgO \cdot 3H_2O + MgO \cdot 4CO_2 \cdot 5H_2O$ found after standing in air	—
$BaTiO_3$	*A*	2.03 pct expansion in a_0	—
	B	2.87 pct expansion in a_0	—
Mica	*A*	Line broadening, 1.3 pct expansion, c_0	0.7
	B	Line broadening, 1.7 pct expansion, c_0	0.6
Plate glass	*A*	No change	1
	B	Dimunition in halo intensity	1
Pyrex	*A*	No change	0.8
	B	Dimunition in halo intensity checked surface	0.55

* $A = 1 \times 10^{20}$ nvt and $B = 2 \times 10^{20}$ nvt. This information was taken from *Solid State Division Report*, ORNL-1852, unclassified.

Table III. Ceramics, Having Low Thermal Absorption Cross Sections, Including Fuel and Fertile Materials

Oxides	Carbides	Silicides
Al_2O_3	Be_2C	$ZrSi_2$
BeO	ZrC	($MoSi_2$)
MgO	(Graphite)	Si
SiO_2		
ZrO_2		
UO_2	UC	USi_2
U_3O_8	UC_2	USi_3
ThO_2		$ThSi_2$

high modulus of elasticity and thermal expansion, it is subject to failure by thermal stresses in reactors operating at very high power. By placing it in metal or graphite containers this problem may be circumvented, and in metal cans fission products may be retained at lower temperatures. ThO_2 has about 78 pct the number of thorium per cubic centimeter as the metal, while the comparable figure for UO_2 is 51.5 pct. The chemical processing of UO_2 and ThO_2 may be accelerated by prior crushing.

Although ThO_2 has the highest melting point of the oxides, a remarkable effect[28] on its sintering at relatively low temperatures was found by adding less than one weight pct CaO. This makes possible the sintering of bulk ThO_2 products in a temperature range used in commercial ceramic firing.

UO_2 Grains—Matrix-type fuel elements requiring UO_2 grains and using various metal clads have been developed. In some cases large dense grains are needed to obtain proper fuel distribution, and in all cases the grains must be sufficiently strong to prevent excessive crushing and reaction during fabrication.

UO_2 in the form of particles of specified sizes may be produced by a number of methods with varying degrees of suitability. Agglomerates of fine UO_2 powders may be made and screened to the desired size. These are then sintered to improve their strength. Fused oxide may be crushed and sieved to the desired particle size. Spray dried UO_3 may be reduced to UO_2, yielding particles which are nearly spherical. Recently a process was developed to produce UO_2 grains (forty to several hundred microns) from UO_2 hydrate crystals. The UO_2 hydrates are grown hydrothermally in an autoclave to a large size, and these are reduced in hydrogen to UO_2 at 1700°C. The resulting particles, shown in Fig. 4, are dense, hard, and of low surface area; they have the same external shape as the UO_3, but are about 2/3 its size.

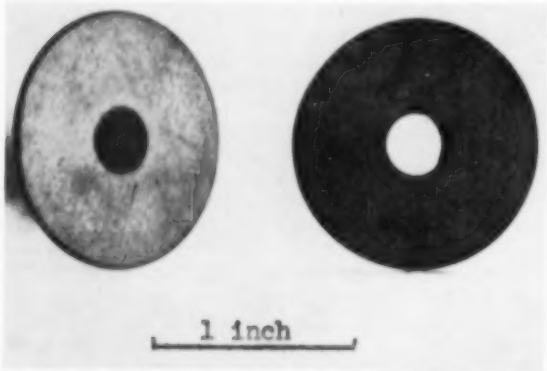

Fig. 5—Cr-Al_2O_3 cermet type fuel elements have been investigated for a number of years.

Cermet Matrix Elements—For high power density and high temperature enriched reactors, the cermet elements are of interest. While there are no cermets developed which are not brittle, many have improved thermal shock resistance and very high strength. They may be fabricated as disks, tubes, plates and other shapes with the uranium fuel compound completely enclosed.

A SiC-Si plate sandwich makes an interesting fuel element. Not only are the thermal and mechanical properties of SiC-Si outstanding, but also the low thermal cross section for neutrons offers the possibility of a fuel element for a high temperature power breeder reactor.

Cr-Al_2O_3 is a cermet which has been intensively developed and investigated for a number of years.[28] UO_2 sandwich elements made of Cr-Al_2O_3 are shown in Fig. 5. While these are part of no specific reactor design, they demonstrate that a suitable shape can be made. These elements are about 0.030 in. thick and 1.0 in. diam. Strung on a rod with spacers, they would make an effective radiator to a gas coolant passing over them. A number of uranium-bearing cermets, including ZrC-Fe and MgO-Ni, have been made.

Conclusions

Ceramic materials offer a possibility for service as high temperature reactor fuel elements. Although much research and development is required, there are a number of ceramics which now may be considered. High temperature radiation damage studies are especially needed.

Ceramics seem particularly suited for use in gas-cycle power reactor systems, and because of the high plant efficiencies possible at high temperatures, it is particularly interesting to consider the role of ceramics in such systems. Some ceramics are useful as reactor fuel elements because they have properties other than their refractory qualities.

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Effect of Nuclear Radiation On Structural Materials

Choice of construction materials for high flux regions of reactors complicated by difficult and costly experimentation required to determine radiation effects and inter-relationship of structural properties in irradiated metals.

by

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ONE of several new considerations in the selection of structural materials for nuclear reactors is the effect of nuclear radiation on the engineering properties of metals. Other conditions that may be experienced in nuclear reactors may also be new in scope or magnitude, so materials selection is doubly complicated since metal properties and service conditions may both be outside the design engineer's experience.

The effects of radiation are reviewed generally and the mechanical properties of carbon and austenitic stainless steels are discussed in detail. It is shown that radiation affects various properties in different ways. The well known inter-relationship between properties for unirradiated metals, that enables us to judge a metal fairly well from a small number of mechanical tests, has not yet been determined for irradiated metals. Therefore, one cannot yet predict the general properties of irradiated metals from a few mechanical tests.

Some instances are shown in which certain metals either fail to meet ASME Boiler Code materials specifications after irradiation or undergo property changes that could be of significance in service but would not normally be detected under existing materials testing specifications.

Some information suggests that, in carbon steels at least, modification of analysis or metallurgical practice may reduce the deleterious effects of irradiation on the ductility of carbon steels.

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At the present time it is believed that results have pointed more toward the need for cooperation between metallurgist, designer, and solid state physicist than toward pessimism about the adverse effects of radiation in reactor structures.

To select structural materials for use in the high neutron flux regions of a nuclear reactor the engineer must consider several novel criteria that are peculiar to nuclear react rs:

1) Materials with low neutron capture cross sections are preferred, because neutron capture by other than the fissionable fuel or the breeding blanket lowers the reactor efficiency and markedly reduces breeding gain or conversion ratio. Low neutron cross section per atom may be an inadequate criterion, and neutron cross section per unit strength, or per unit corrosion resistance may have to be considered.

2) Bulk heating resulting from the attenuation of gamma rays in the material, gradients in the bulk heating, and potentially high rates of bulk heating can give rise to thermal stresses and higher rates of applications of these stresses in reactor materials than have been commonly experienced in other structures. Gamma-ray heating may exceed several watts per gram in high flux reactors, and reactor power changes by a factor of 100,000 in one second have been produced.

3) Materials with high thermal neutron capture cross sections must be avoided where subsequent transmutations change the nature of the material by transmuting a critical alloying element to another element that is not metallurgically comparable.

Otherwise very long exposures to high neutron fluxes may result in an alloy of different composition and properties.

4) The material must be resistant to deleterious radiation effects. Energetic (fast) neutrons in a reactor have the ability to change the properties of a material by introducing vacant lattice sites, interstitially placed atoms, momentary high temperature regions (thermal spikes), or by breaking chemical bonds. Consequently many of the important engineering properties, or behavior characteristics, may be affected, some adversely.

In addition to the above requirements it should be recognized that several secondary problems are posed:

1) Suitable experimentation to test or to develop materials with characteristics that are suitable under reactor operating conditions is expensive, difficult, and time consuming. The work is hampered by the shortage of experimental facilities in high-flux experimental reactors and lack of sufficient laboratory facilities to carry out the testing of the radioactive, irradiated materials. This means that engineers must learn to make their decisions from a much smaller body of data than that to which they have been accustomed.

2) The meaning of the same mechanical test, as it bears on service performance, may not be the same for irradiated and unirradiated materials, because irradiation can alter not only the measured values of the various mechanical properties, but also the familiar relationship between these properties and their response to small changes in testing procedure.

3) Extreme condition of corrosion, chemical environment, temperature, etc. may further limit the selection of materials.

4) Because of potential hazards to personnel and property, leaks cannot be tolerated in systems containing radioactive materials, and the possibility of catastrophic failure of large parts, such as pressure vessels, must be minimized to the vanishing point. This requires built-in integrity and added factors of safety that may be difficult to reconcile with high performance and economic design and operation.

5) Inspection and maintenance of reactor vessels cannot be made by conventional methods because of the radiation levels after operation. Either complex and expensive inspection means must be devised or a new order of ability to assure long life must be achieved.

The first group of requirements set out above is rather severe, but it must be obvious that at least one class of materials, metals, and alloys is generally capable of meeting these requirements, because there are in existence a number of successfully operating nuclear reactors. However, if our plans for economic nuclear power are to mature, it will be necessary to devote increased attention to the understanding of metals and alloys under reactor operating conditions so that we may be able to develop superior materials to meet the more exacting demands of the future.

It is the purpose of this paper to discuss the radiation effects aspects of the metallic materials problem in nuclear reactors.

Testing and Evaluation of Irradiated Metals

The problems and difficulties encountered in attempting to obtain adequate information about irradiated materials are many. At the outset, one is handicapped by not knowing what properties or tests are most important or meaningful. The tests to be performed and the alloys to be examined must be carefully selected both to estimate the validity of the tests and to determine how typically the few pounds (or even ounces) of test specimens selected may represent all metals commercially produced to the same nominal specification.

The mechanism of radiation effects, while it is understood qualitatively, has not lent itself to detailed quantitative treatment.[1-6] Vacancies, interstitial atoms, and probably some form of localized lattice heating are causing the property changes, but it is not known what defects, or what agglomerations of defects, are causing the different property changes. As yet sufficient details are not known on the effect of temperature on the stability or the state of the defects.

Understanding of radiation effects is hampered by the unhappy state of knowledge of the solid state in the absence of radiation, and ignorance is particularly great where structure sensitive properties are concerned. Fortunately, the rate of progress during the last few years bodes well for the future. In spite of these difficulties, a number of patient investigators have collected much useful information over the last several years.

Types of Experiments: Irradiation experiments may be of two types: in-pile, where the important measurements are made in the reactor during actual irradiation, and pre-post, in which all measurements are made outside the reactor before and after irradiation. Dynamic properties such as creep and fatigue should be determined by in-pile experiments. In-pile experimentation is both difficult and expensive. Drastic miniaturization of test specimens and apparatus is usually required; instrumentation and transducers tend to be more subject to radiation damage than the metallic test specimens; gamma ray heating in high flux reactors increases the difficulty of operating isothermal tests; and the number of tests is severely limited by space in the high flux reactors.

Pre-post experiments are simpler, but gradients in both the gamma ray heating and the neutron flux make it difficult to carry out isothermal, equal flux irradiations on more than a handful of specimens at any one time. In addition, they tend to become excessively complicated if exposure to specific environments is required during irradiation.

The work of post-irradiation testing of most irradiated metals must be done in a shielded enclosure, variously referred to as a cave, hot-cell, or simply cell. Many testing operations may be carried out in cells at very nearly the same rate as outside, but such preliminary tasks as removing specimens from the apparatus in which they were irradiated, or the placing together and measuring the elongation on a broken tensile specimen may take inordinate numbers of man or cell hours. The solution appears to be better design and more complete remote and automatic controls for testing machines and their auxiliaries.

Experimental Variables: Neutron Flux: In addition to the usual variables that must be controlled in

any metallurgical experiment, testing under irradiation requires measurement and control of neutron flux. The neutron flux (neutrons per sq cm per sec) gives the rate of bombardment with neutrons, and the (time) integrated neutron flux or integrated flux is the product of the neutron flux and the length of irradiation. The integrated flux thus represents the amount of bombardment by neutrons in neutrons per sq cm (or the conventional symbol nvt).

Radiation effects may depend on either or both the flux and the integrated flux. Two specimens irradiated to the same nvt (integrated flux), one by a low-flux, long-time irradiation, the other by a short-time, high-flux exposure, may not be in the same state. This fact reduces the opportunities for extrapolation of data, and possibly decreases the validity of accelerating tests by employing fluxes substantially greater than may be encountered in service.

The energy of the neutrons whose numbers are given by the flux is important; except for transmutations, it is believed that all the radiation effects in metals are caused by relatively high energy, or fast, neutrons. The usual convention is to call neutrons with energies greater than 1 mev fast neutrons. The convention is not universally accepted, and because determination of fast neutron flux is at present a rather involved process, fast flux values in the literature may not be reliable.

The range of fast neutron fluxes in experimental reactors ranges from about 10^{10} to 10^{14} neutrons per sq cm per sec at present, and fluxes in excess of 10^{15} are not unforeseen in power reactors. When one considers that a power reactor may be required to operate ten years or more, and that it demands a great deal of patience and money to sit out a one-year-long experimental irradiation, it may be seen that the gap between experimental and service exposures may be a factor of 100 to 1000 in integrated flux. The great bulk of the data today is for exposures between 10^{18} and 10^{20} nvt.

Experimental Variables: Temperature of Irradiation: Particular attention is called to the temperature of irradiation as an experimental variable. Thus far a great deal of the data on irradiated metals has been obtained from experiments irradiated near room temperature or other convenient temperatures that usually do not coincide with projected reactor operation. That temperature of irradiation could influence results had long been expected, but only recently has it been demonstrated that irradiation temperature can be so important. First, since many radiation effects can be annealed by time and temperature, it would be expected that the higher the irradiation temperature the less would be the effects of irradiation. This has been found true. But, diffusion-dependent metallurgical reactions that are accelerated by irradiation have been found to depend on the temperature of irradiation. For instance, although accelerated aging in solution-quenched, precipitation-hardenable copper-beryllium alloys may be easily observed during irradiation at 80°F,[4] the effect cannot be observed at a much lower irradiation temperature.[5] Thus, the irradiation at a low temperature may cause a large number of lattice defects to be retained unannealed and influence but little the metallurgical changes, while irradiation at a higher temperature may be sufficient to anneal lattice defects but speed metallurgical changes.

From the foregoing considerations and data to be presented below it is plain that future materials irradiations must be carried out over the range of service temperatures, although, as has been pointed out, this may be difficult to do without reducing the number of specimens that can be irradiated.

Physical Properties

Except for electrical resistivity, few of the physical properties of metals have been measured after long irradiations. Electrical resistivity measurements on pure metals under cyclotron and reactor irradiation are numerous, because there has been much interest in fundamental studies of the behavior of defects that contribute to the residual resistance of metals at low temperatures. Although large changes in residual resistance have been measured at low temperatures, the resistance changes in metals at room temperature and above have generally been only a few percent.

Only one measurement of thermal conductivity under irradiation has been reported: the conductivity of nickel at 1470°F which was observed not to change.[6] Because of the parallel behavior of electrical and thermal conductivity at reactor temperatures in metals, the electrical resistivity data indicates that substantial changes in thermal conductivity will not result. The radiation induced defects that cause the changes in electrical resistivity tend to anneal at much lower temperatures than the defects that cause changes in the mechanical properties. To anneal the defects causing the yield point elevation in copper requires about 570°F, but annealing of most of the electrical resistivity effects occurs much below room temperature.

Recent experiments have shown that irradiation of less than 10^{18} nvt can cause changes of several percent in Young's modulus of copper.[7] It was also observed that there was a very marked decrease in damping capacity. D. O. Thompson[7] believes that this is due to defects pinning down dislocations originally present in the material.

Table I. Pre and Postirradiation Values of Hardness, and Yield and Tensile Strength of Various Alloys*

	Rockwell Hardness No.		Yield Strength, Psi		Tensile Strength, Psi		Ratio of Yield Strength: Tensile Strength	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post
2SH14 aluminum	8F	40F	18,000	23,000	20,000	27,000	0.9	0.85
2SO aluminum	—	—	7,000	17,000	17,300	26,000	0.51	0.65
High purity iron	—	—	18,000	31,000	36,000	37,000	0.5	0.84
Normalized carbon steel			50,000	93,000	75,000	97,000	0.67	0.96
Hardened and tempered alloy steel	—	—	153,000	196,000	164,000	198,000	0.93	0.99
Austenitic stainless steel	81B	99B	37,000	97,000	98,000	115,000	0.38	0.84

* Data for the table were compiled from refs. 12, 13, 14, 16, and 22.

Density and dimensional changes have been sought in a number of irradiated materials. As a rule, any changes observed in metals have been so small as to approach the experimental error of the determinations in the pure metals and simpler alloys. Density decreases have been reported for stainless steels by a number of sources;[9,8] the changes have been on the order of 0.1 pct. More substantial density changes have been observed in materials with other than metallic binding. Density changes of several pct may be caused by irradiation of diamonds,[10] and a 0.3 pct density decrease has been observed in titanium carbide.[11] This expansion of essentially nonmetallic phases in the metallic matrix of an alloy is a possible cause of secondary radiation effects, because a highly stressed or strained region of an alloy could result from the expansion of a disperse phase.

There has been no indication to date that any of the physical properties of metals tested will experience serious changes after irradiation. It is only the damping capacity that has showed large decreases (in copper single crystals), but the engineering significance of this would not be great except in very special instances. In addition, it is far from certain that engineering materials, in which the damping capacity is very much less than in annealed copper to begin with, will experience changes as large as were observed in copper.

Mechanical Properties

Irradiation induced mechanical property changes can be substantial and possibly of sufficient magnitude to influence materials selection and design.

Fig. 1—Comparison of characteristic conventional stress-strain curves for irradiated and unirradiated alloys is shown. 1) Behavior of austenitic stainless steels:[13] note dependence of yield stress and shape of curve on strain rate. Similar yield point behavior has been observed in 2S aluminum,[15] copper,[17] nickel,[14] and high purity iron.[15,19] 2) Behavior of normalized carbon steel:[12] note elimination of pronounced yield point; and curve shape for irradiated steel is similar to irradiated metals in No. 1.

First, the radiation effects on the individual properties will be described in a general way and later certain types of alloys will be considered separately.

Strength and Hardness: Increased strength and hardness almost invariably result from neutron irradiation of metals if the temperature of irradiation or test is not so high that the radiation induced defects are annealed. Generally, annealing of the radiation effects in metals occurs substantially below the recrystallization temperature in engineering alloys.

Starting with a given base metal, it may be hardened or strengthened by alloying, metallurgical treatments, or deformation. Experience shows where the limits of strengthening by these various means will lie. Irradiation will, in general, be able to add strength to metals in almost any condition, but like most strengthening mechanisms in metals, the action is more potent in the softer starting materials. Also it does not appear that irradiation can cause much greater strength than can be achieved by other means except in an alloy where the potential of increased strength by working cannot be realized because of lack of ductility. In this case irradiation may be able to harden to a greater extent than other means commonly at our disposal.

The extent of hardness and strength increases in a number of metals is shown in Table I. It will be noted that the yield stress is generally elevated to a greater extent than the tensile strength, and this causes the yield and ultimate strength to approach very closely. Obviously, then, the rate of work hardening between yield and ultimate must be very low or the plastic extension prior to necking will be very small.

The manner in which plastic deformation begins in irradiated metals is unusual in many cases. Mild steels that characteristically show a yield point at the onset of plastic deformation do not generally show a yield point after irradiation.[12] Instead, continuous yielding is followed by a region of low work-hardening, a point of inflection, and an increase in hardening followed by the usual decrease in work hardening up to the maximum load. On the other hand, the face-centered cubic metals acquire a yield point after irradiation if the strain rate is sufficiently high; at lower strain rates the stress strain curve assumes the same shape as that for irradiated mild steels.[13] Fig. 1 shows this behavior graphically. To date these yield point phenomena have been observed in austenitic stainless steels,[13, 18] 2S aluminum,[15] nickel[14] and copper.[17] For the austenitic stainless steels at least it has been shown that the yield stress is strongly strain rate dependent,[18] although this is not the case in unirradiated alloys of this type.

Because the manner in which plastic deformation begins is unusual in many of the face-centered-cubic metals, and because there is a strong strain-rate dependence of the yield stress in metals that normally do not have such properties, the designer and the metallurgist should re-examine their conventional mechanical tests in terms of expected service conditions. In a structure in which any relief of an overstress by plastic deformation is required, the irradiated metal, because of its higher yield stress, may not deform but may be stressed to a higher level and acquire additional strain energy that could be released at an inopportune moment. Because there are frequently steep flux gradients in and near

reactors, the extent of hardening by radiation may vary greatly in short distance. From this arises the possibility that an overstress in one part of the system may be transferred to another unexpected region because of the different properties that the irradiated metals have acquired, although they may be physically very close together and in the same state before irradiation.

Ductility and Toughness: The reduction of area and the elongation measured from tensile test specimens is usually reduced in irradiated metals. In some pure metals and in a few other age-hardenable or cold-worked alloys, irradiation may actually increase the elongation. While the ductility figures from the tension tests are probably not as important as the ones determined by notch-bar impact testing, they nevertheless give some indication of the ability of a metal to withstand a reasonable amount of plastic deformation before fracture. Metals with low initial ductility seem to suffer greater reductions in ductility than materials of generally high ductility. Increased ductility, after irradiation, has been noted in two cold-worked aluminum alloys (A54S and 52SH34)[16] and in two age-hardenable nickel alloys (Hastelloy C and K Monel) irradiated at 540°F.[17]

Table II. Pre and Post-Irradiation Ductility Values of Various Alloys*

	Elongation up to Maximum Load, Pct		Conventional Elongation, Pct		Reduction of Area, Pct	
	Pre	Post	Pre	Post	Pre	Post
					(sheet specimens)	
2SO aluminum	—	—	38	21	—	—
2SH14	—	—	22	20	81	75
Normalized carbon steel	22	5	—	—	65	26
Austenitic stainless steel	49	25	—	—	71	62
QMV beryllium	—	—	1.4	0.2	—	—
356 aluminum	—	—	2.7	0.6	—	—
Molybdenum	—	—	44	0	68	0

* Data were compiled from refs. 12, 13, 14, 16, and 22.

Normalized carbon steels of the type used for pressure vessel construction suffer serious ductility loss after irradiation. In molybdenum alloys the same effect has been observed,[18] but high-purity iron loses little ductility after irradiation.[19,13]

The austenitic stainless steels, the tougher nickel base alloys, and a number of nonage-hardenable aluminum alloys seem to lose very little ductility in irradiation, but there are examples of aluminum base (356)[12] and nickel base (K Monel) alloys,[17] rather low in initial ductility, that have lost substantial amounts of ductility. Table II shows typical ductility values for a number of metals.

In considering the reduced ductility of the more ductile metals, it must be remembered that simultaneously an increase in yield and ultimate strength accompanies the loss in ductility in the irradiated metals. If two reasonably ductile annealed metals are brought to the same yield stress level, one by cold work, the other by irradiation, it will usually be found that the elongation and reduction of area are greater for the irradiated metal, but the ultimate strength of the cold worked metal may be greater or less than the irradiated metal.

Creep: The effect of radiation on creep has been reported recently both under neutron and heavy, charged-particle irradiation. The work on copper[20] and aluminum[21] in the cyclotron has been at rather high strain rates to be considered of technological importance, but the work on aluminum[22] was at rates of more general interest. Of these experiments none showed any substantial effect of radiation; so, the results are essentially negative, but, nonetheless, important. Some unpublished work done on austenitic stainless steel at Oak Ridge[23] has shown that the radiation effects are a function of temperature (and presumably of the stress level or creep rate). Decreased creep rates (by a factor of two) were noted at 1200°F under irradiation, but at higher temperatures (with the same stress, and thus a higher creep rate) irradiation caused a lesser reduction in creep rate. Slight increases in creep rate have been observed at 1500°F. Because there are so many variables affecting creep, and because the sign of the effects of a given variable may be different under various conditions, it is not possible to generalize on creep results more than to say that no serious deleterious effects of radiation have thus far been observed.

Siegel and Billington[24] ran some simple stress-relaxation tests on a few alloys some years ago. In these tests, conducted at high stresses and low temperatures, it was observed that radiation increased the rate of stress relaxation. Almost certainly the presence of the defects that cause increased yield and tensile strength should slow creep at lower temperatures where deformation takes place in a similar manner to low temperature plastic deformation. The effect of thermal spikes might, however, be able to speed the deformation process by activating atoms in highly stressed (on an atomic scale) regions of a metal.

One factor that has been examined only superficially is the effect of radiation on the ductility in creep, or the time for fracture, or perhaps the time at which third stage creep begins. Even if the preponderance of data should show that the creep rate is unaffected or reduced by irradiation at temperatures at which some measurable radiation effects were manifested in lowered ductility or increased strength, it appears prudent to determine whether irradiation might not shorten the useful creep life of a structure by so reducing the ductility that fracture would take place prematurely.[25]

Radiation Effects in Specific Groups of Materials

Austenitic Stainless Steels: The austenitic stainless steels have many outstanding properties that have made them so popular. Superficially, irradiation does not seem to have greatly reduced their utility for nuclear reactor service. The question is: "Have we run the proper tests to determine their fitness under these unusual conditions?" Some of the characteristics of the mechanical behavior of these steels after irradiation are known.[12,17] The yield stress may increase by a factor of three, the ultimate stress by 25 pct, and the uniform elongation may be reduced by one half. The reduction of area is decreased as little as two and as much as 20 pct. The area under the stress strain curve is not greatly affected. In addition, the yield stress becomes strongly strain rate dependent, and a five fold increase in the strain rate elevates the yield stress at least 5 pct after 10^{19} nvt. At 10^{20} nvt the percent-

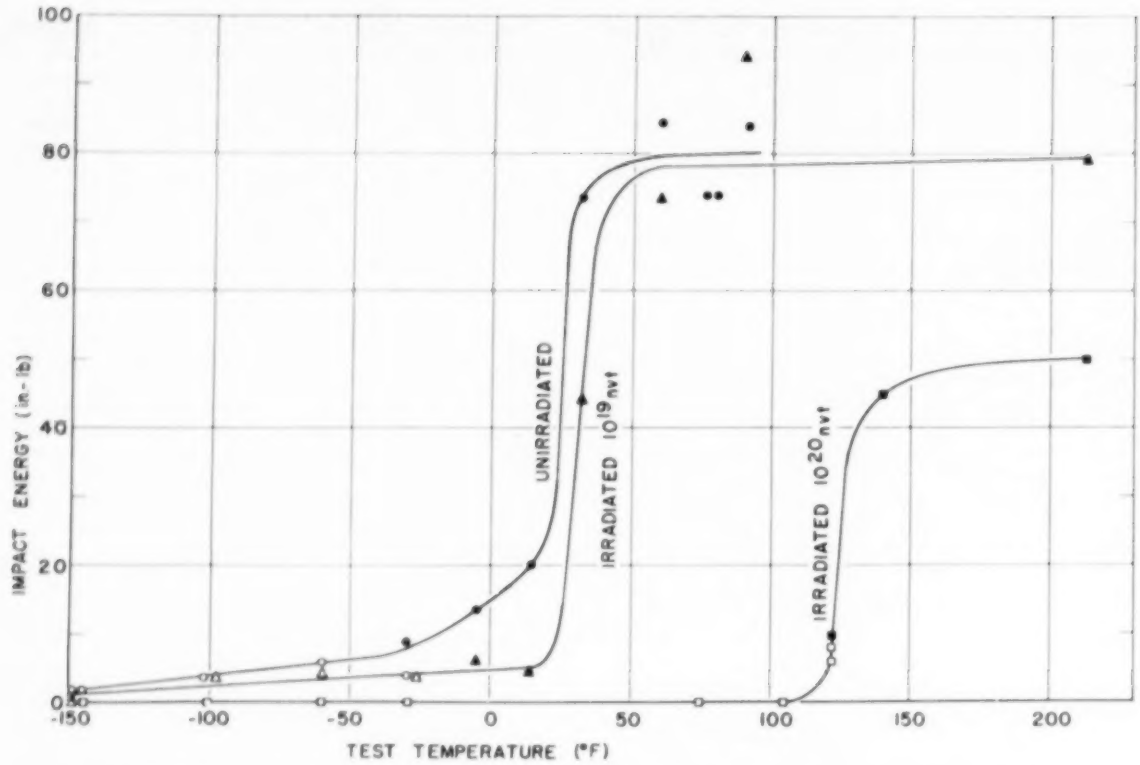

Fig. 2—Effect of irradiation on notch-impact properties of a normalized ASTM A-212 grade B steel. Subsize 0.2 in. square Izod specimens were used. Note that irradiation induced shift in curves to higher temperatures is greater at lower energy levels.[11]

age increase is slightly greater, but because the yield stress is almost twice as great for the higher irradiation, the difference in stress is greater. Exposure to 10^{20} nvt increases the hardness substantially above the maximum limit allowed in a typical ASTM specification (ASTM A-240). Also Reynolds[10] has shown that radiation slightly increases the ferrite content of type 347 stainless steel.

Essential information that is not known includes the following: What is the effect of irradiation temperature on the annealing of damage, the rate of ferrite formation, and the tendency to form σ or precipitate carbides; why do the ductility properties vary so greatly (compared to strength changes) in different steels as a function of irradiation; what will be the effect of test (or service) temperature on the properties that have, to date, been determined only at room temperature; what will be the effects of manganese and chromium depletion and vanadium buildup from transmutations?

Because materials specifications are generally founded on a less than scientific basis it is not certain that even if a steel were developed that was able to meet all the specification tests in the irradiated condition that it would perform as well in pressure vessel service as the unirradiated steel.

The ASME Boiler Codematerials specifications show that irradiated stainless steels have properties that may not pass the specifications test or that could lead to variable results when tested within the limits specified. It appears possible that some of the irradiated metals may not be able to show the minimum elongation required. The limits on testing speed for tensile and bend tests are rather broad, and speed definitely affects the yield stress in the irradiated steels. Speed effects on the ductility of unirradiated steels are also well known; it is not known how irradiation may complicate this already complex subject. The purpose of this example has been to demonstrate the fact that the Boiler Code materials specifications, a well considered and practical work (which was never intended to be used for irradiated materials) that serves industry so well may not be a reliable guide to the selection of materials for reactor service at high fluxes, although it is the best categorized and codified guide.

To evaluate a stainless steel for reactor service it is obvious that more test data will be required. This data and the design characteristics of the reactor structure will then have to be compared to see whether the conditions to be met in service, the range of variable of stress, strain, and temperature and their time rates of change, have been sufficiently well covered by the testing program. From the meager data at hand, it appears that consideration must be given to two of the more obvious phenomena that arise in irradiated metals that are not characteristic of unirradiated metals. One, because speed effects appear pronounced in the irradiated material, and because high rates of stressing are sometimes achieved in reactors, the range of speeds of stressing or straining in reactor operations must be carefully estimated, and the metallurgist must key his test to conditions that represent the extremes of the variables the designer can predict for service. And, two, the temperature of irradiation and test should be near the expected service temperature because there are several possible metallurgical reactions that radiation may affect in addition to its influence on the annealing of defects.

Carbon Steels: The general effects of irradiation of normalized carbon steels, such as might be used for pressure vessel materials, are shown in Table III, where the properties of an A-212 Grade B steel are compared. After 10^{20} nvt it will be noted that the steel exceeds the specification values for maximum tensile strength, and in all probability the elongation falls short of the specification value. If the radiation effects are judged from the notch-impact properties, a shift in fracture transition temperature of over 100°F is observed after 10^{20} nvt, Fig. 2.[12] If the shift in the curves is measured at some arbitrary low energy level, a more realistic approach in the light of current thinking on unirradiated metals, the spread (in temperature) becomes considerably greater than for the fracture transition temperature.

The effect of temperature of irradiation on the carbon steels is not well known. It has been shown that higher irradiation temperatures, on the order of 570°F, result in lower yield stress elevations than if the irradiations are carried out below 200°F,[12] but simultaneously the tensile strength was found less sensitive to irradiation temperature. Indeed, there is some evidence that the higher irradiation temperature produced a higher tensile strength (and lower elongation and reduction of area) than a lower temperature irradiation.[12] Sutton and Leeser showed that irradiation at 425°F was capable of causing an equal or greater shift in transition temperature than irradiation at 580°F. The effect on the yield stress of iron of annealing after irradiation has been shown by Kunz and Holden,[18] and the process appears to be fairly simple.

Experience with notch impact tests on high purity iron and a number of steels at Oak Ridge National Laboratory has indicated that the effects of irradiation on the impact properties vary greatly.[28] High purity iron and quality steels, such as A-212 and A-106, appear to be less affected than steels of lower quality and higher sulfur and phosphorus contents. The differences are noted both in the amount of shift of the fracture transition temperature and in the reduced energy required for fracture above the transition temperature.

From the foregoing remarks, it may be seen that the radiation effects in carbon steels are dependent on a number of known and probably unknown factors. It appears possible to irradiate a steel (A-212 for instance) only sufficiently to keep the properties within the ASME Boiler Code materials specifications and yet have the impact properties shifted to an extent that may endanger service performance. Since the boiler code does not call for impact tests for vessels to be operated above −20°F, it appears prudent to require such tests for irradiated metals, because of the changes in relationships between the various mechanical properties that irradiation is capable of causing. Also it is a matter of conjecture whether a given impact value at the same temperature for two similar steels, one irradiated, one not, gives the same assurance of protection from brittle fracture in service for both.

The tentative observations that composition strongly influences the impact behavior of irradiated steels gives some hope that improved resistance to deleterious radiation effects can be achieved by variations in alloying and steelmaking practice.

Because much of the notch impact data on irradiated metals has been obtained from subsize specimens, and because standard impact data for irradiated metals could not be quantitatively interpreted if it were available, the data so far obtained can only serve as guide to the significance of the radiation effects. If the effects are really bad, there appears to be hope of mitigating the effects by the design of alloys or selection of service temperature. At the moment what is most needed is a clear idea of the relationship between test and service performance for carbon steels. With this as a basis it might be possible to plan adequate tests for unirradiated materials. In the interim, Charpy V-notch and drop weight[29] tests appear to be the most fruitful tests. In addition, it is believed that the effect of speed of deformation should be investigated for the irradiated metals, and, as should be obvious by now, irradiation and testing near service temperatures should be mandatory.

The use of some of the newer high strength steels for reactor vessels is attractive in many ways. A reduction in wall thickness may be achieved that is greater than would be anticipated from the increased working stress alone, because of the marked reduction in tangential thermal stresses brought about by the thinner wall. Another gain may be made in reducing or eliminating the thermal shield and reducing in the poisons in the reactor, especially in the case of a converter or breeder where the neutron economy is of such great concern. However, since code decisions on some of the newer materials are recent or pending, their usefulness is not yet well established. The effects of radiation, also, must be studied. Leeser and Sutton[17] showed that the hardness of the harder steels is increased only slightly by irradiation, but in a quenched and tempered high-strength steel it has been observed that yield stress and ultimate stress increases of 20 pct are common at very high strength levels, although the tensile ductility suffers appreciably. The yield and ultimate stress often will be within 1 pct of each other.

Table III. Effect of Irradiation on Mechanical Properties of ASTM A-212 Grade B Carbon Silicon Steel[12]

	Yield Strength, Psi	Tensile Strength, Psi	Reduction of Area, Pct	Uniform Elongation, Pct, to Necking
Unirradiated	50,000	75,000	64	22
Irradiated 10^{19} nvt at 140°F	65,000	81,000	68	18
Irradiated 10^{19} nvt at 570°F	57,000	84,000	57	12
Irradiated 10^{20} nvt at 175°F	94,000	97,000	26	5

Other Metals of Interest: There are several metals of particular interest to reactor designers that may become important. Beryllium, titanium and zirconium alloys have certain properties that are unique, but all three of these materials are normally used with a hexagonal-close-packed structure. Not only are radiation effects data scanty, but also the integrity of these materials as structural components in large sections has yet to be evaluated for metals with the hexagonal-close-packed structure.

Beryllium, although it can scarcely be considered as a structural metal, is an excellent moderator and thus may be required to operate in the highest flux regions of a reactor. The thermal stresses may be of sufficient magnitude to require some plasticity in

this metal of low ductility. The yield strength of beryllium after an irradiation in excess of 10^{20} nvt (fast)[24] has been known to increase from 24,000 to 50,000 psi, and the tensile strength increased from 35,000 psi to the same value as the irradiated yield stress. The elongation, initially 1.4 pct, decreased to 0.2 pct.

The high corrosion resistance of titanium has suggested its use in reactor, although the cross section is rather high. Notch impact tests on iodide process metal or the alloy Ti-75A after an irradiation of about 10^{20} nvt[25] have disclosed no deleterious radiation effects.

Zirconium alloys, combining potentially good corrosion resistance and low neutron cross section, are being actively developed by Westinghouse[26] specifically for nuclear reactor use. Insufficient data are available to assess the notch-impact properties of the irradiated metal after 10^{20} nvt.[26] The yield and tensile strengths are appreciably elevated by irradiation.

Bruch and others[27] have shown how the transition temperature of molybdenum (in tension) is elevated by neutron irradiation in a manner analogous to the carbon steels. Judging from the behavior of the carbon steels it does not seem unlikely that proper composition or metallurgical practice could improve the resistance to radiation effects.

Summary

The properties of engineering interest in a wide variety of materials have been reviewed as they are known to be affected by irradiation. In addition, some of the possible implications of the property changes have been pointed out, and logical paths for future research have been deduced from the limited data at hand.

Comparing what is known and what should be known, new emphasis on the following three principles appears to be required for judging the importance of radiation effects:

1) Tests should be re-examined to see if they subject metals to conditions that are new in scope or magnitude because of the unique conditions that may exist in nuclear reactors.

2) The irradiation and test temperatures should be close to service temperatures.

3) Added emphasis should be given to solid state, metallurgical, and mechanics research to aid in extending or extrapolating data to conditions of neutron exposure that do not appear to be attainable in sufficient time to give all the necessary data to the reactor designer.

Conclusions

Attempting to predict the effects of radiation on a metal is difficult, while changes from a few percent to perhaps a factor of three may occur in the various properties, it has, in many cases, been observed that the magnitude and direction of the change in these properties occur separately or independently in a manner that is new compared to the way the properties may be changed by variations in analysis, metallurgical practice, working or heat treating. Adverse (or beneficial) changes in the properties of structural metals brought about by irradiation generally do not appear large or significant for any one property. It is rather the combination of new and different values for the various properties that makes one hesitate to approve a given metal for reactor applications. It is believed that radiation effects in metals have the potential of making some metals unsuitable for reactor service, although they may be suitable in the absence of irradiation. To determine whether this potential will be realized is extremely important and exceedingly costly. The answers are important to the builder, the operator, and the insurer of a nuclear reactor.

It has not been the intent of the authors to be overly pessimistic about the effects of radiation on metals. The desire has been to show that there are still many materials problems remaining to be answered before the reactor designer can proceed with complete confidence in the reliability of many of our commonly used metals and alloys. Present experience seems to indicate the desirability of research leading to development of metals and alloys with properties particularly suited for reactor use. It should be re-emphasized that neutron irradiation effects are unique in that they cannot be duplicated by any other presently known techniques, such as cold working, heat treatment, or alloying, for manipulating the properties of metals and alloys.

It is believed that the job can be accomplished in time to assure satisfactory service if there is no failure on the part of the reactor designer, metallurgist, or solid-state physicist to cooperate fully in presenting and understanding each others viewpoint throughout the research and testing programs.

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Preprecipitation Phenomena In Supersaturated Solid Solutions

by A. Guinier

PRECIPITATION in alloys is undoubtedly one of the most essential phase transformations in metallurgy and, besides, it is a phenomenon of great interest to physicists. It seems then that it can be chosen as a topic for an Annual IMD Lecture. Of course, the subject is a very wide one and I shall discuss here only a very restricted part of it. I should like to show why it is now considered that there is, at the beginning of the process, a stage distinct from the real *precipitation*, which is the *preprecipitation*. We shall be chiefly interested in the atomic structure of the metal in this preprecipitation stage.

Numerous reviews on this subject have been published recently.[1-3] The latest was given by H. K. Hardy[3] at the last meeting of the Institute of Metals in London. One of the most complete articles has been written by the late Dr. Geisler.[4] I should like, at the beginning of this lecture, to pay a tribute to the memory of our friend Arthur Geisler. Some of the ideas which will be developed here are different from those advocated by him. But everybody knows the considerable progress in experiment and in theory which we owe to him and, personally, I deeply feel how fruitful have been the long discussions which we have had during many years.

Experimental Basis of the Precipitation Problems

Let us recall the essential facts pertaining to the problem of the precipitation. The starting point and the final one are well known. The initial stage is the supersaturated solid solution before quenching. The dissolved atoms replace some of the atoms of the solvent at the points of a definite lattice. It is generally considered that the distribution of the atoms is completely random, and that the lattice distortions are relatively weak. These assumptions are only an approximation. It has now been proven[5-8] that, in some cases, the dissolved atoms have a tendency to segregate to form very small nuclei. These fluctuations of composition are greater than the normal statistical fluctuations in a purely random alloy. We shall see the role played by these nuclei later.

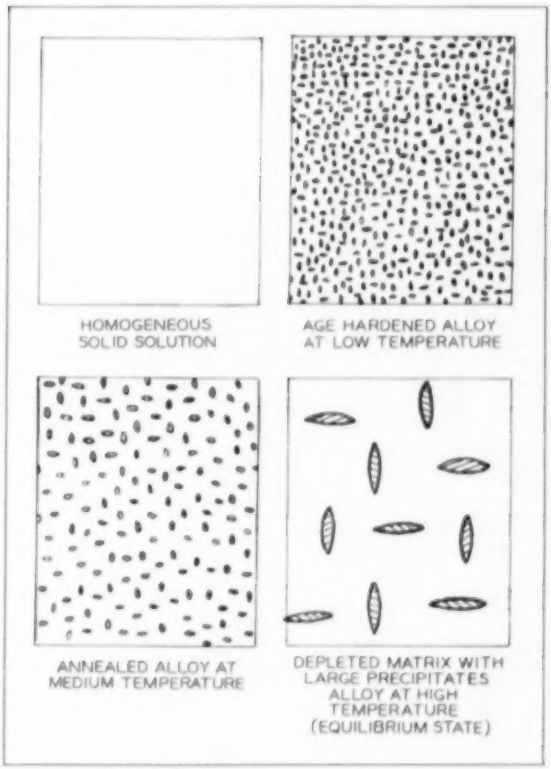
HOMOGENEOUS SOLID SOLUTION
AGE HARDENED ALLOY AT LOW TEMPERATURE
ANNEALED ALLOY AT MEDIUM TEMPERATURE
DEPLETED MATRIX WITH LARGE PRECIPITATES ALLOY AT HIGH TEMPERATURE (EQUILIBRIUM STATE)

Fig. 1—Scheme of the successive structures of a supersaturated solid solution from the homogeneous stage to the precipitated stage is illustrated.

The final state is obtained by a very long annealing at such a temperature that an equilibrium is reached in a reasonable time. The alloy is then composed of a matrix which is a saturated solid solution, much poorer than the initial one. Imbedded

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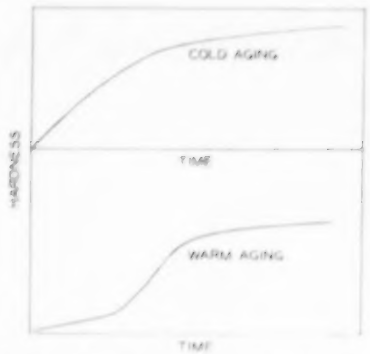

Fig. 2—Schematic hardness curves for cold aging and warm aging are plotted.

in this matrix are the grains of the precipitate indicated by the equilibrium diagram.

In the transformations which we shall consider here, the crystal of the initial solid solution retains its identity up to the end of the precipitation. Its external shape and its orientation remain unchanged. There is only a possible variation of the lattice parameter, generally very small. That means that there is no complete reorganization of the atoms, but only a rearrangement of solute atoms in a practically fixed lattice.

Our task is to describe the intermediate steps between these two stages and, if possible, the paths actually followed by the atoms. If the annealing is made at progressively lower temperatures, the processes are slower and slower. However, according to the equilibrium diagram, one would expect no change except in the kinetics of the transformation. Nevertheless, the precipitation phenomena are generally profoundly changed. The first possible change is that another form of precipitate can occur. This fact is easily visible on micrographs or X-ray patterns. It is interesting to note this point here, because we shall discuss analogous but more subtle changes later.

Let us suppose now that we keep the annealing

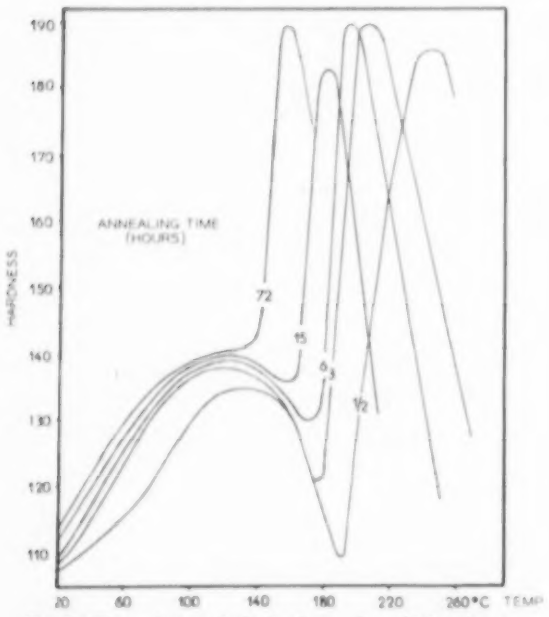

Fig. 3—The variation of the hardness of an Al-Ag alloy is plotted against annealing temperature for a given annealing time.[11]

temperature in a range narrow enough always to have the same precipitation phase. Let us say, for instance, Al_2Cu θ' in an Al-Cu alloy. It is found that at a given temperature, after a short annealing, we have numerous small precipitates; after a long annealing, large and less numerous precipitates, Fig. 1. When the temperature is increased, a similar coalescence occurs. Inversely, when the temperature of annealing is progressively decreased, the precipitates cease to be visible with the optical microscope, though they are still detectable with the electron microscope. Rough evaluations lead to the conclusion that the total amount of the precipitated phase rapidly approaches the equilibrium value. It is chiefly *the distribution of the precipitates* which varies in large proportions. From the beginning of the process of precipitation, a large fraction of the dissolved atoms is eliminated from the matrix in a large number of small particles. While the annealing continues, most of the initial particles redissolve to the benefit of others, which grow.

Let us now anneal the alloy at a low temperature, below 100°C for Al-Cu; or let us age it at room temperature. No precipitate can then be detected with the ordinary techniques or with the electron microscope. On the usual X-ray diffraction patterns, there are neither new lines nor spots which could be attributed to the lattice of a precipitated phase. Nevertheless, the properties of the alloy, mechanical or electrical, are quite different from those of the quenched state.

We are faced here with the old problem of age hardening. What is the structure which explains the properties of the metal when no precipitation can be detected?

Sequence Theory of Precipitation

An idea, which seems quite natural, comes from an extrapolation of the interpretation of the direct observations. There is still a precipitation from the very beginning of the process, but the particles are so small that they are well below the resolving power of the replica techniques of the electron microscope. The particles are also so small that their diffraction lines are very broad, and thus so weak that they cannot be detected in powder diagrams. In fact, ordinary patterns of the age hardened alloys showed nothing else than the lines of the matrix. The situation changed in 1938[5, 6] when refined techniques were used—single crystal specimen and strictly monochromatic radiation. Diffuse spots and

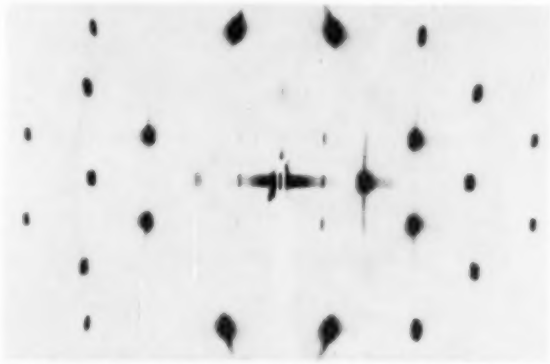

Fig. 4—An example is given of the diffuse scattering characteristic of the preprecipitation stage. The Al-Cu single crystal was aged for two days at 100°C. MoKα radiation was used with the oscillating crystal.

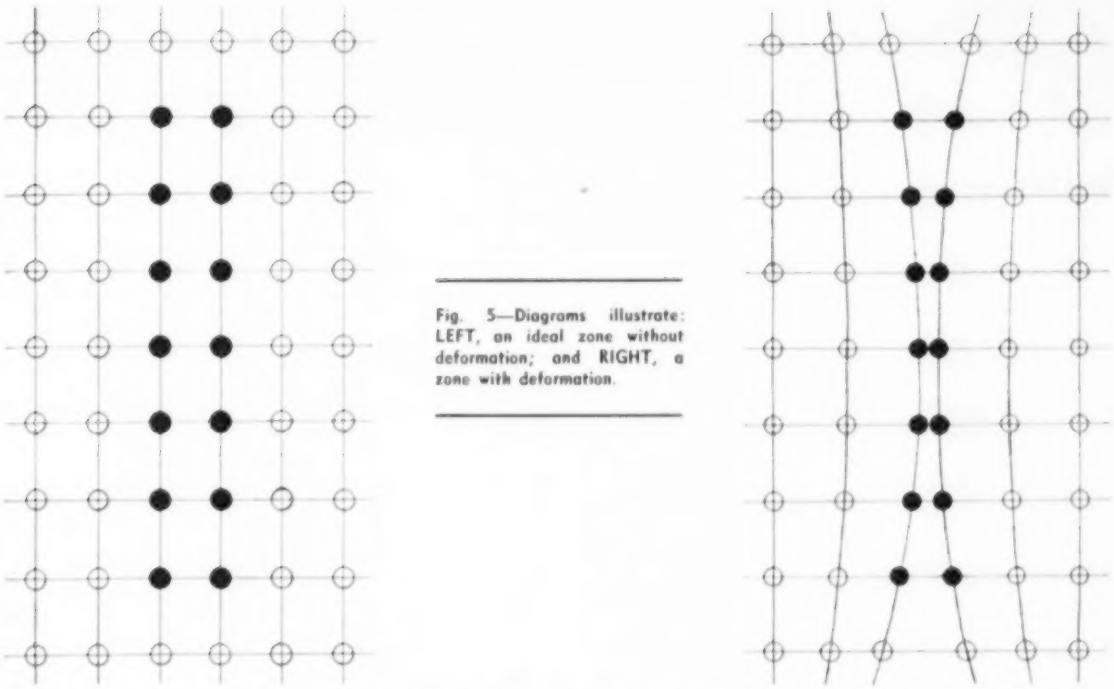

Fig. 5—Diagrams illustrate: LEFT, an ideal zone without deformation; and RIGHT, a zone with deformation.

streaks were found in addition to the Bragg spots of the matrix with an age hardened Al-Cu alloy. Later, similar effects were observed in many age hardening light alloys and in Cu-Be.

One possible way of interpreting these observations was to suppose that these diffuse spots are diffraction spots of a crystalline precipitate, so small that they are considerably broadened by the well known size effect. The shape of the broadened spot is determined by the shape of the diffracting grain. This was the foundation of the sequence theory developed by Geisler.[9] The precipitate would grow continuously from a submicroscopic size. From the evolution of the shape of the diffuse spots during the aging, Geisler concluded that the growth of the precipitate was anisotropic. At first, the nucleus grows in one direction, forming a needle. Then the needle develops into a platelet. Finally, the platelet thickens. Geisler added that it was possible that the lattice of this precipitate is different from the known form, which is observed when the grains have a microscopic size.

This simple theory of the continuity of the precipitation process has been recognized as insufficient in the majority of cases, and has been replaced by the more complicated scheme of preprecipitation. This theory has been introduced: 1) to explain the evolution of the properties of the alloy; 2) to give a correct interpretation of the diffuse scattering of X-rays. The essential point which we shall emphasize is the following assumption. *There is no real precipitate* in the first stage of hardening but small heterogeneities of the solid solution called *zones*, without a characteristic crystalline lattice.

Physical Evidence for the Preprecipitation Stage

More than twenty years ago, long before the study of the structure of zones by X-rays, the idea of discontinuity in the precipitation process had been put forward by metallographers such as Dehlinger.[10]

The age hardening process is considered the result of two phenomena, more or less distinct, according to the conditions of the annealing. They have been called *cold hardening* and *warm hardening*, because the easiest way to pass from the first to the second is to increase the annealing temperature. This idea is supported by the following observations:

1) The kinetics of age hardening is different at low and high temperatures. At elevated temperature, there is an incubation period followed by an accelerated hardening. The *sigmoid* curve is characteristic of a nucleation and growth process. But in the *cold hardening*, the hardness curve is nearly linear near the origin and the rate of hardening is continuously decreasing, Fig. 2.

2) Köster and Coll[11] have drawn the isochronal curves for the Al-Ag alloy relative to different properties, mechanical and electrical, Fig. 3. These curves give the value reached after a given time of annealing plotted against the annealing temperature. The curves present two maxima, separated by a well marked minimum. For instance, for ½ hr the alloy is softer at 200°C than at room temperature. This softening separates the domains of the cold and the warm hardenings. The treatment which suppresses the cold hardening is the retrogression treatment, a few minutes at 200°C, now widely used in the light alloys industry. It is effective in the majority of age hardening alloys, and this retrogression is not easily understood if the idea of a continuous process is used. It would be necessary to suppose that *all* the small precipitates redissolve during the short treatment at 200°C. It is improbable that the unstable small precipitates have the same internal structure as the stable larger ones, above a well defined temperature.

It is fairly certain that the structure responsible for the second stage of hardening, the warm hardening, is the true precipitate.[12, 13] Since the properties of the metal in the first stage are quite different, and since there is a discontinuity between the two stages, we can conclude that the first stage is not a precipitation. This is confirmed by the X-ray

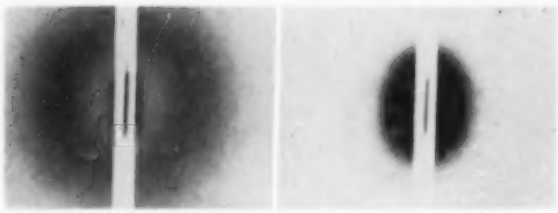

Fig. 6—Small angle scattering by an age hardened Al-Ag alloy is shown a) as quenched, small zones; and b) annealed 1 hr at 205°C, large zones.

results on the atomic structure of the alloy at this stage.

X-Ray Evidence for the Preprecipitation Stage

As has already been said, the characteristic feature of the X-ray diffraction patterns of an age hardened alloy is the diffuse scattering. In the last years, considerable progress has been made, both in the experimental techniques and in the theory of diffuse scattering. We shall not give details here, but simply discuss the results.

The aim of the experimental X-ray work is the determination of the reciprocal space of the crystal. Let us say that for a perfect crystal, the reciprocal space contains only the points of the reciprocal lattices of the different phases. These points correspond to sharp Bragg spots.

The reciprocal space of the age hardened alloy in the preprecipitation stage contains: 1) the reciprocal lattice of the matrix, and 2) domains of diffuse scattering of various shapes and dimensions. They correspond to the broad diffuse *anomalous* spots or streaks observed in addition to the normal Bragg spots. An example of these streaks is shown in Fig. 4. Their intensity is always *much weaker* than the Bragg spots.

According to the sequence theory, it would be necessary for the center of these diffuse spots to be at the points of the reciprocal lattice of a definite crystalline phase. The critical objection against this theory is that, in the case of the best known systems, it is impossible to find such a lattice.[14] On the other hand, the diffuse scattering may be correctly interpreted as due to a kind of imperfection of the matrix lattice, which we shall call *zones*.

Nature of the Zones

We suppose that, as in the true precipitation process, the dissolved atoms in the supersaturated matrix have a tendency to segregate. But the zones, i.e., the small domains where the concentration of soluted atoms is high, *have no proper well defined crystalline structure*. The simplest hypothesis is to assume that the atoms remain at the points of the lattice of the matrix, Fig. 5a. Such a zone will be called *ideal*, because the lattice is not deformed or very little deformed. This model is satisfactory in some systems when the atoms have nearly the same diameter, such as Al-Ag or Al-Zn. A slight deformation can thus be expected, even in regions with an anomalously high concentration of dissolved atoms.

Generally, however, a gathering of dissolved atoms inevitably produces strong distortions of the lattice. In the zone, the atoms are then removed from the matrix points, Fig. 5b, but it is characteristic of the structure of the zone that they do not reach any regular arrangement. In other words, the structure of the zone may be regarded as a more or less strongly distorted matrix lattice. The distortions may vary from the center to the periphery of the zone in proportion to the concentration of the dissolved atoms. Therefore, the zone has no well defined boundaries. There is a perfect coherence between the zone and the surrounding matrix. Nevertheless, in an approximate way, one may speak of the shape of the dimensions of the zone.

Such a structure can exist only if all the atoms of the zone up to its center are strongly influenced by the lattice of the matrix. That is, a zone is stable only if it is very small, especially when the deformations are important. The order of magnitude of the observed zones is 100A or less. The shapes of the zones are different in various alloys. Zones have been found in Al-Cu for the first time. In this alloy, they are platelets parallel to the (100) planes. They are now often called Guinier-Preston zones. But this is only a particular case. The word *zone* is used here in a more general sense.

A coherent block of the matrix crystal contains a great number of zones randomly scattered and probably of statistically varying sizes. These local imperfections alter the periodicity and thus give rise to a diffuse scattering outside the normal Bragg reflections. To calculate this scattering, the zone cannot be isolated. The whole matrix lattice with the embedded zones has to be taken into account. This type of calculation is possible, but the important problem is the reverse one: deducing the structure of the zones from the observed scattering phenomena. It is a difficult problem and it is not possible to find a general solution.[15] Let us recall that, even for perfect crystals of known composition, crystallographers have not yet a general method to find the position of the atoms in the cell. But the present problem is much more complicated, since the lattice is irregular and the composition of the zone unknown.

Up to now we have generally tried to imagine a model of structure and to compare the theoretical and the experimental repartition of diffuse scattering. We shall not discuss these crystallographic problems, but rather insist upon some results which now seem established beyond doubt, and which are of interest for the metal physicist. The zones ob-

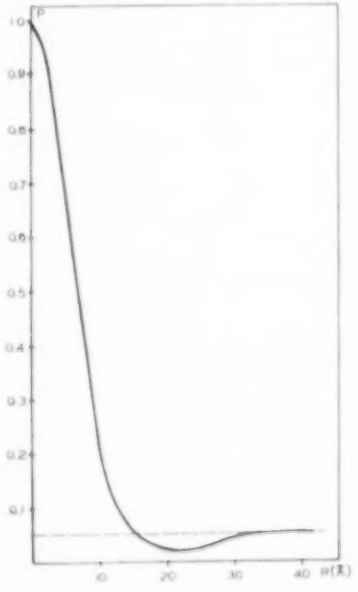

Fig. 7—Concentration of silver as a function of the distance to the center of the zone is plotted.

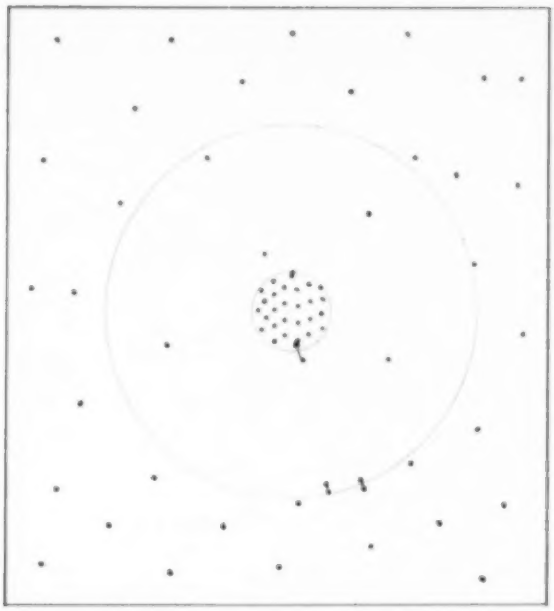

Fig. 8—The formation of a complex zone is illustrated.

served in various alloys can be classified into a few general types, which we shall describe.

Zones Without Lattice Distortion

The most striking example is found in Al-Ag. This system is of special interest, because the two atoms have nearly the same diameter, and a different scattering power. Thus, they are easily distinguished by X-rays. In the preprecipitation stage, the characteristic of the diffraction pattern is a circular halo of small diameter around each node of the matrix. The more easily visible halo is found around the center of the reciprocal space, Fig. 6. Recently, this phenomenon has been extensively studied,[15, 16-18] and good agreement has been reached as to the observations and structure. The silver atoms remain on the points of the matrix lattice. The zones have a spherical symmetry, at least statistically. Through a Fourier transform of the scattered intensity, the concentration of silver is found as a function of the distance to the center of the zone.[17] Therefore, the zone is formed of an enriched nucleus surrounded by an impoverished shell, Fig. 7. The excess of the silver atoms in the central part is exactly equal to the defect in the outer part. The dimensions of the zone can be determined in absolute value. They vary with the annealing conditions, and are of the order of 10 to 40A. However, it is not possible to find the absolute value of the concentration. Gerold[16] showed that experiment gives, without any prior hypothesis, a *segregation degree* which is the product of the total volume of the zones by the proportion of gathered silver atoms in each of them.

This type of zone, the structure of which is clearly revealed by X-rays, had been independently imagined by theoreticians. According to Dehlinger,[19] the segregation in the cold aging stage leads to *complexes;* i.e., two adjacent domains, one enriched and the other impoverished. He has studied thermodynamically the stability of these complexes.

Qualitatively, at least, the formation of this zone can be well explained. As was said earlier, in the solid solution in equilibrium at high temperature, there are already small silver rich nuclei. At low temperature, after quenching, the tendency to segregation is higher because the solution is supersaturated, but the mobility of the atoms is low. The silver atoms which are in the immediate vicinity of a suitable embryo migrate towards this embryo by an *uphill diffusion* process. The driving force is due to the difference between the free energy of the atom in the matrix and in the nucleus. This lowering of the free energy may be attributed to the valence electrons, because here the elastic strains are negligible. It is also possible that some kind of order exists between silver and aluminum inside the nucleus.[20] When a silver atom, jumping from one site to the other, comes in contact with the nucleus, it has a good chance of remaining at this nucleus, Fig. 8, so the surrounding layers are progressively emptied of silver. They could be refilled at the expense of the matrix by the process of the normal *downhill diffusion.* However, the driving force in the case of diluted solid solutions is due to the concentration gradient and the diffusion is very slow, as shown by the value of the diffusion coefficient extrapolated at low temperature. Thus, the impoverished shell does not disappear; and the nucleus stops growing when the thickness of the depleted shell is large enough for a silver atom from the matrix to have a negligible chance of reaching the nucleus through the shell.

If the annealing temperature is increased, the mobility of the atoms becomes higher and the zone can grow. When the zones are large—for instance, for Al-Ag at 180°C—the small angle X-ray pattern is formed by a central spot rather than by a ring, Fig. 6b. That means that the central nucleus is not surrounded by a well defined shell any more, because the diffusion is easier. At still higher temperatures, let us say above 220°C, the stability of the nucleus becomes insufficient, and the zones dissolve by diffusion. The silver atoms must be engaged in a particle of the true precipitate, with a much lower free energy, to be able to resist the dispersive action of the normal diffusion. So we will go from the domain of the cold aging with zones to that of warm aging with precipitates.

This qualitative picture shows that during the formation of the zone, the movements of the atoms occur on very small distances—about 10 to 20 atomic distances. If the rate of formation of the zone is calculated with the usual diffusion equations, a time would be found of hundreds of years instead of a few minutes.[21] We have seen that the formation of the zone is the result of two diffusion processes. The diffusion of silver atoms from the matrix towards the outer part of the zone is very slow, but the diffusion towards the nucleus is much faster. Nevertheless, in both cases, the general diffusion equations are correct, though the gradient of concentration must be replaced by the gradient of the thermodynamical potentials. For diluted normal solid solutions, the activity coefficient is nearly equal to the concentration, but in the highly concentrated nucleus it is probably very different; hence, the increased rate of diffusion. On the other hand, between the diluted solid solutions of the outer shell and the matrix, the ratio of activities is nearly equal to the ratio of concentration and so, as expected, diffusion is very slow.

Zones of the Al-Ag type have been found in other systems where the lattice distortions are small, i.e., when the atoms are nearly the same size. It is

interesting to compare the behavior of these light alloys to that of an apparently different alloy, Cu-Ni-Fe. The alloy of composition Cu_2Ni_2Fe, has been studied by Daniel and Lipson,[13] and by Hargreaves.[14] Above 900°C, there is one phase with a cubic lattice. The quenched single phase alloy is decomposed by an annealing at about 800°C into two tetragonal intermediate phases, one copper-rich and the other copper-poor. Both have the same parameter *a*, but the axial ratios are respectively greater and slightly less than unity. This stage of decomposition—rather than precipitation because, here, no phase is preponderant—is preceded by another stage, analogous to preprecipitation. It is characterized by a X-ray pattern exhibiting an anomalous scattering effect. The diffraction lines of the cubic matrix are accompanied by two symmetrical satellites of very weak relative intensity, which are called *side-bands*. These side-bands have been found in other alloys, like the nimonic alloy (80 pct Ni-20 pct Cr, with aluminum and titanium), Fig. 9a.[14]

Hargreaves successfully interpreted his observations with a model of *modulated structure*, based on a periodic arrangement of alternate copper-rich and copper-poor lamellae. The side-bands are the consequences of the variation of the interplanar distance in the two series of lamellae. The period, which determines the separation of the *side-bands*, was found to vary from 60 to 130A, according to the heat treatment.

It is difficult to justify the existence of so large a *periodicity* with respect to the interatomic distances. Moreover, it is found that this *periodicity* would change gradually when the alloy is annealed at a higher temperature. However, this transition cannot be made without a complete reorganization of the atoms, which is difficult to imagine. Actually, it seems that a periodically modulated structure is not necessary to account for the side-bands.[15] It can be replaced by an ensemble of complex zones distributed at random in the solid solution. A zone, Fig. 9b, is formed, for instance, by one copper-rich lamella between two impoverished lamellae, the copper atoms migrating from the outside towards the center. Such a zone gives rise to side-bands. This is demonstrated by an optical analogy. Fig. 9c is the optical diffraction pattern of a linear grating containing a defect, as drawn in Fig. 9b.

The distance of the satellites to the normal lattice point gives the thickness of the zone. When the side-bands come closer to the normal lines, it means that the zone is growing, and it is no longer difficult to understand the gradual modification. The scattering phenomena are quite different from those observed with Al-Ag. They are due not to variations of scattering power, but to variations of the lattice parameter. On the other hand, the shapes of the zones are different. They are platelike, parallel to (100) planes. In their essential features, however, the structures of the preprecipitation stages are analogous. The mode of formation and growth of the zone by local movements operate on the same principle. The zones are larger because the annealing temperatures are much higher. Hence, the diffusion paths may be longer.

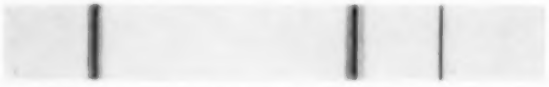

Fig. 9a—Photograph shows example of side-bands given by nimonic alloy.[14]

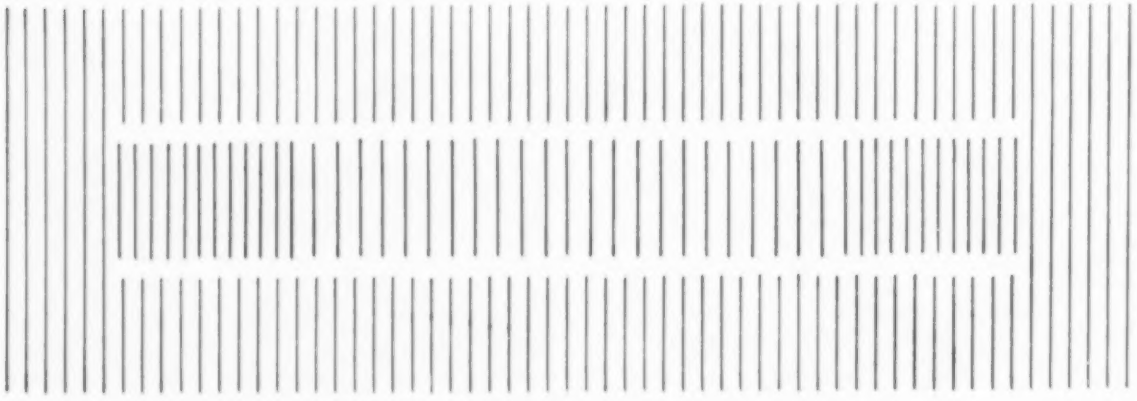

Fig. 9b—A model of a complex zone formed by 24 dilated planes between 12 contracted planes is drawn.

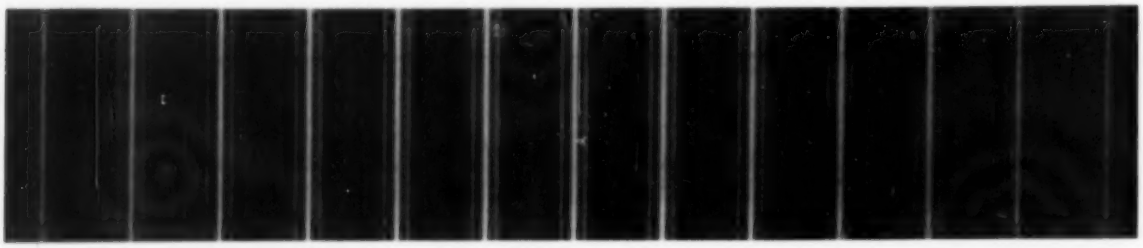

Fig. 9c—Photograph shows optical diffraction model of zone 9b, showing side-bands near each diffraction line, according to M. Françon.

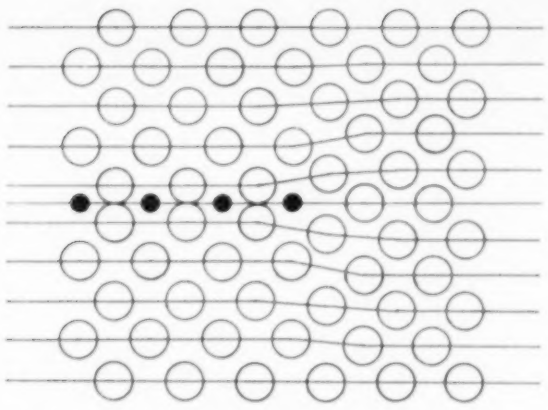

Fig. 10—Illustration shows model of a Guinier-Preston zone in Al-Cu according to Gerold.[39] Open circle represents aluminum atom, filled circle, copper atom.

Zones With Strong Distortions

The best known zones of this type are found in the Al-Cu alloy, 4 pct Cu. Many papers[38-39] have been devoted recently to the Guinier-Preston zones of Al-Cu. Nevertheless, although a number of facts are definitely established, we are not yet in a position to give a thoroughly quantitative description of these interesting structures.

The zones are plane and parallel to the (100) planes of the matrix. They are primarily caused by a gathering of copper atoms in small regions of certain (100) planes. The diameter of the zones, which varies with the aging treatment, is of the order of 100A. Their thickness is much smaller, only a few interplanar distances. The observed scattering phenomena cannot be explained by any repartition of aluminum and copper atoms if they are supposed to be placed at the points of a regular lattice. Lattice deformations must be introduced, which can thus be considered as experimentally proven. Since the copper atoms are smaller than the aluminum atoms, the atomic planes adjacent to the copper-rich plane may be imagined as coming closer than the normal. The simultaneous occurrence of atomic displacements and of variation of scattering factors makes this theory difficult to prove. The schematic model of the zone, Fig. 10, based on Gerold's investigation,[39] is in qualitative agreement with the observations, but it cannot be considered as definite. The dimensions of the zones cannot be determined without somewhat arbitrary hypotheses, and the exact proportion of segregated copper atoms is still uncertain. But it is very probable that when the aging, even at room temperature, is practically finished (2 days), more than half of the copper atoms are concentrated in the zones.[39]

In spite of this considerable depletion of the matrix, the lattice parameter of the matrix does not change. Furthermore, the diffraction lines are as sharp as the lines of a sample of pure, perfectly annealed aluminum.[39] From the width of the line, the minimum size of the coherently diffracting domain is calculated as greater than 3000A, while the mean distance between zones is of the order of 100A. A great number of zones are thus included in the elementary block. X-rays measure the average of the interplanar distances taken in the entire block. The local irregularities due to the zones give rise to diffuse scattering at large distances from the lattice points in the reciprocal space, but do not broaden the points themselves. This is the best proof of the coherency between the matrix and the zones. The behavior of the matrix diffraction line is quite different, where there are true precipitates.[39]

Although the size of the zones is greater than the limit of resolving power of a good electron microscope, the ordinary etching techniques do not reveal these zones.* Castaing, using a transmission method,[35] seems to have succeeded in obtaining an image of the zones, Fig. 11, when these zones are as large as possible—long annealing at 100°C. The black points correspond to a concentration of copper, more absorbing for the electrons. They are of the expected magnitude, and disappear when the specimen is heated at 200°C—retrogression phenomenon.

* When the Al-Cu alloy contains zones, *white points*[31,35] are observed on electron micrographs. However, these points are not a direct image of the zones.

Let us compare the Al-Cu to the Al-Ag zones. What is the origin of the differences which are observed? The most striking fact is that in Al-Cu, there is no experimental sign of a well defined impoverished region around the nucleus of high concentration. It must be concluded that the normal diffusion is sufficient to smooth down the gradient of concentration between the matrix and the outer part of the zone. On the other hand, the solid solution is much more diluted in the case of the copper alloy—maximum of 2 instead of 13 atomic pct for Al-Ag. If, in a (100) plane, the copper concentration reaches 30 pct, at least the seven adjacent planes on both sides have been completely emptied of copper. Thus, the diffusion seems to be easier for the copper atoms than for silver. Nevertheless, the normal diffusion coefficients of silver and copper in aluminum are of the same order of magnitude.

It is possible to attribute this different behavior to the distortions which are very strong around the nucleus of copper and very weak in the silver alloy. Jagodzinski and Laves[31] think that the rate of diffusion is greater in a strained region. More precisely, Turnbull[34] supposes that the dislocation lines form

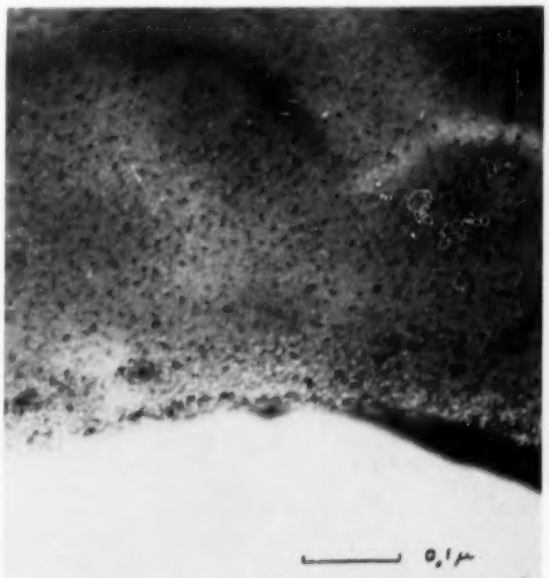

Fig. 11—Electronmicrograph of an Al-Cu alloy aged ten days at 100°C[35] was taken by the transmission method.

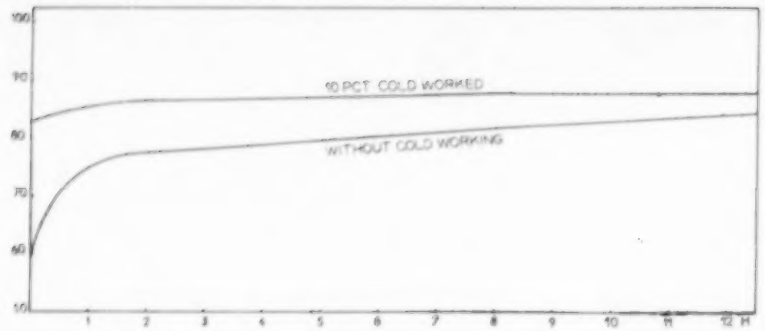

Fig. 12—Hardness curves for an Al-Cu alloy are plotted with and without cold working, after quenching.

channels for the copper atoms and make a short circuit for the atoms through the lattice.

There is also a difference between the origin of the driving forces in the two types of zones. The embryo of a zone with distortion may be a defect in the lattice, as a clustering of vacancies or dislocations. An important fraction of the diminution of free energy would be due to the interaction between the dissolved atoms and the defect, not only to interaction between these atoms and the solvent atoms.

A number of experimental facts seem to prove the influence of the lattice defects on the Guinier-Preston zones.

1) The zone has a peculiar shape in direct relation with the matrix crystal, whereas the zones without distortions are quasi-spherical. Hirano[30] supposes that the copper atoms are attracted by a cluster of vacancies parallel to the (100) planes. Some authors explain these differences without reference to lattice defects. Mott and Nabarro[26] explained the plate-like shape by strain energy, and Smoluchowski[27] tried, from the calculation of elastic strains, to foresee the habit plan of a flat zone.

2) The distortion of the lattice after quench has a considerable influence on the subsequent aging. It has been found[27] that the hardening is quasi-instantaneous after the deformation, Fig. 12. It is too intense to be accounted for simply by the straining of the crystal. There must be a change in the constitution of the solid solution. In fact, X-ray patterns show the existence of very small Guinier-Preston zones.[30] The number of defects is much higher than in the undeformed metal, and they rapidly attract the copper atoms situated in their immediate vicinity, forming a small zone. The development of the normal larger zones is hindered because the majority of the copper atoms already are in a rather stable position. That explains why the hardening seems to be stopped at room temperature, Fig. 12. After an annealing at moderate temperature, 100°C, the copper atoms are liberated from the unstable small zones and certain zones are allowed to grow. The hardening of the coldworked metal is thus retarded.

3) The development of the zone is faster when the quenching is more drastic, Fig. 13. Quenching strains cannot be invoked, because the effect of the deformation has been shown to be the reverse. The important factor is perhaps the greater number of quenched vacancies.[30] Seitz[31] feels that they accelerate the rate of diffusion. According to Hirano,[30] they also increase the number of embryos of zones.

From these various facts, it may be concluded that the lattice defects play an essential role in the deformation and stability of the Guinier-Preston zones. This shows how difficult any precise calculation would be. Thermodynamical computations based only on the variation with concentration of the energy of the normal lattice or the quasi-chemical approximation become of doubtful validity.[31-33]

Other Types of Zones

The X-ray investigation of different age-hardening alloys has revealed the existence of zones whose structure is certainly very different from those just described. But a complete interpretation of the observed diffuse scattering has not yet been given and the structure of these zones remains obscure. Let us give a few examples.

In the ternary alloys Al-Mg-Si and Al-Ge-Si, the

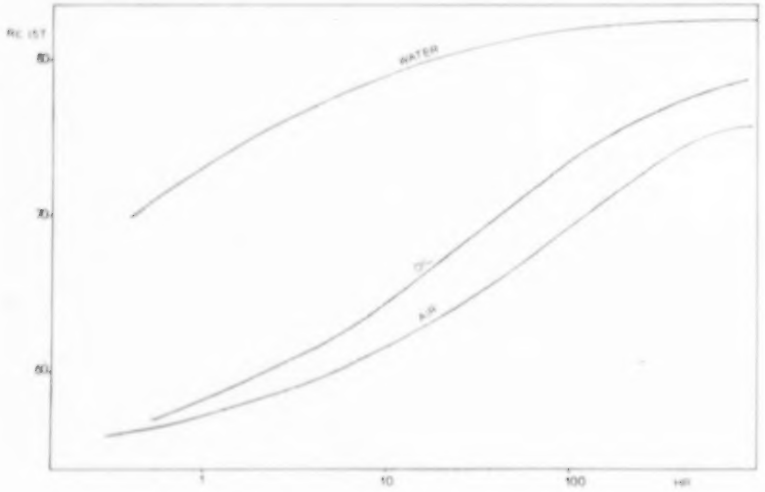

Fig. 13—Hardness curves of an Al-Ag alloy aged at room temperature are plotted for different ways of quenching.

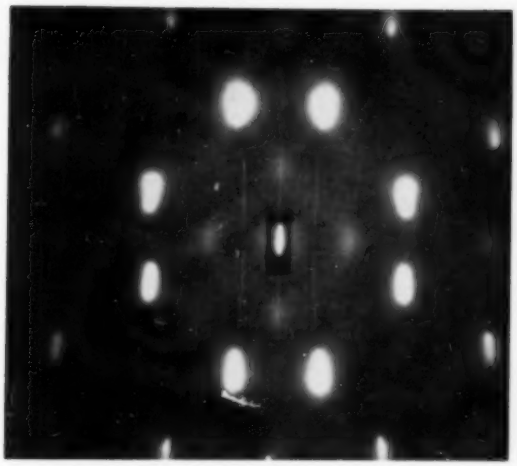

Fig. 14—Diffuse scattering by an Al-Mg-Ge single crystal with a [100] axis along the X-rays MoKα, aged 1000 hr at 150°C, is shown.[44]

characteristic feature of the preprecipitation stage, Fig. 14, is a zone in which the periodicity is preserved in only one direction, the [100] axis. This is about all we know with certainty.[44] The zone is probably needleshaped. It is interesting to observe that, in the true precipitation stage, many precipitates are long needles parallel to the [100] axes.[45] There is an obvious relationship between the habits of the two segregation processes. Let us recall that in Al-Cu, the zones are parallel to (100), and the precipitates Al_2Cu θ' appear with a very marked Widmanstätten structure, along the same planes. The anomalous scattering effects are equally well visible in Al-Mg-Si, where the atoms have the same scattering power as in Al-Mg-Ge when there is a strong contrast. It can be concluded that lattice distortions are important, but we do not know their nature. One may imagine that they are related to the formation of chains of Mg,Si or Mg,Ge, in which the bonds are not truly metallic, but rather ionic.

Another example of a still mysterious preprecipitation stage is encountered in the Al-Cu-Mg[46] and Al-Mg-Zn systems.[47] Diffuse round points are observed whose relation to the matrix reciprocal lattice is not evident. In this particular case, perhaps these points could be explained by reference to very small particles of a precipitate with a distinct lattice. The preprecipitation stage is not yet proven, except perhaps at the beginning of the hardening at room temperature. It must be noted that the well developed precipitate has no simple relations of epitaxy with the matrix.

This example shows how diverse the processes of precipitation are. Any generalization made hastily would be dangerous.

Comparison of the Formation of the Zones And of the Precipitates

Various authors[8, 47] have shown how the changes of the different properties can be explained, even in detail, by the successive stages of the preprecipitation, and of the precipitation with different forms of precipitates. These different stages replace each other according to the annealing conditions.

We shall relate here only the differences between the kinetics of the two principal stages to the atomic structures of the zones and the precipitates.

The nucleation and growth process in the precipitation has been studied theoretically and experimentally, and is well known. The characteristic parameter is the energy of formation of the stable nuclei. This energy comes from the energy of the boundaries between the particle and the matrix. It is large when the lattice of the precipitate is not coherent with the matrix, because many atoms in the transition layers are in a position of high energy. Precipitation cannot take place when the temperature is low, because there is no chance for a group of atoms of the supersaturated solid solution to get an excess of energy sufficient to overcome the potential barrier of the stable nucleus.

On the other hand, zones have only a very small surface energy, because there is, in fact, no real boundary around them. The formation of the zones is then very easy. Therefore, they are numerous, and there is practically no incubation time. One could say that the critical radius of the stage nucleus is very small. Thus, the zones are formed even at low temperatures, in spite of the small gain of free energy.

When the temperature is raised enough to allow the appearance of some nuclei of the precipitate, the growth of the precipitates at the expense of the zones represents a decrease for the free energy of the whole. Thermodynamically, it is possible that the zones redissolve and that the dissolved atoms migrate towards the precipitate. This is the transition between the cold hardening and the warm hardening.

This transition may occur not only by the elevation of the annealing temperature, but for any cause which makes the nucleation of the precipitate possible. Thus, a severe coldwork of the metal produces disordered domains with excess energy. It has been observed[48] that in the Al-Cu alloy, after a cold rolling of 90 pct, the Al-Cu θ' phase appears after a few minutes of annealing at 150°C, whereas normally the Guinier-Preston zones are formed and grow for many hours.

The presence of impurities may also produce a transition between two modes of hardening. This is the case with Al-Cu-In alloys.[49]

Conclusion

Neglecting all the still ill-understood details of the observations and the uncertainties of the tentative theories, we may retain a simple but firm conclusion. The precipitation is not a continuous process. The segregating atoms may form different structures. During the passage from one to the other, the major part of the first redissolve and atoms migrate towards the nuclei of the second. Are the nuclei of the new structure formed at the segregates of the previous structure? It is possible, but the question does not have much meaning. In any case, the majority of the first segregates disappear. The successive structures are characterized by a free energy, smaller and smaller per atom, with an increasingly higher nucleation energy. The zones constitute the first stage. Then one or several kinds of precipitates may appear, the first being the most coherent with the matrix.

The zone has a nonperiodic structure, with lack of periodicity due either to the nature of the atoms or to their positions. It must be considered as a large defect in the matrix lattice. Progress both in the theory and in the technique of X-rays makes an analysis of the structure of the crystalline imperfec-

tion possible. We have shown some of the first results, which already seem well ascertained. But there is still much worthwhile work to be done in this field. Every metal physicist is now interested in lattice imperfections. Unfortunately, in pure metals the distorted regions are very small, and we still lack experimental means for a direct study of these structures. The theoreticians use a great deal of imagination, or at least they use the elements which are now most fashionable among their colleagues; dislocations, vacancies, etc.

But zones are giant defects. We have some precise information on their atomic structure and a rapid progress may be expected. On the other hand, zones have a predominant influence on many properties of metal. Thus, they constitute a good opportunity for the theoretician to verify his theory on an experimentally known imperfect structure.

Acknowledgments

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Separation of Germanium and Cadmium From Zinc Concentrates by Fuming

Vapor pressure determinations were made on synthesized germanium sulfides. Germanium and cadmium were removed from sphalerite concentrates by fuming. The fume was retreated to separate some of the cadmium from the germanium and, at the same time, upgrade the germanium to more than 5 pct content.

by H. Kenworthy, A. G. Starliper, and A. Ollar

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MANY sphalerite concentrates contain certain impurities which have economic value as by-products. These may include the volatile sulfides of germanium, cadmium, and lead. The objectives of the research reported in this paper were to study the fundamental volatility characteristics of germanium sulfides, to increase the recoveries of ger-

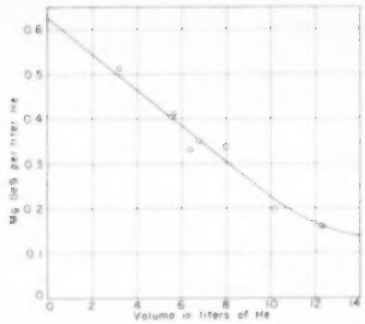

Fig. 1—Graph plots extrapolation to saturation curve for GeS at 400°C.

manium and cadmium compared to smelter recoveries, and to develop an effective method for separating the bulk of the germanium from the cadmium. These studies are in part a continuation of those previously published in a Bureau of Mines report.[1]

Laboratory scale extractive experiments were conducted on zinc concentrates procured from the Minerva Oil Co. operations in the Illinois-Kentucky fluorspar district.

Vapor Pressure Investigations

Nearly pure GeS and GeS_2 were prepared, using procedures based on the work of Johnson and Wheatley.[2]

GeS_2 was obtained by conversion of GeO_2. GeS was prepared by partial reduction of GeS_2. As shown in Table I, both products varied slightly from theoretical analyses.

Vapor Pressure of GeS—The vapor pressure of GeS was measured by the vapor saturation method, which consists of heating the material under investigation in a moving stream of neutral gas and determining the weight of material that would be in a measured volume of saturated gas. The amount of GeS vaporized was measured by the weight loss of the sample in a moving stream of helium at two or more rates of flow. Computation of weight loss at the saturation point of the helium was made by extrapolation to zero rate of flow. The values obtained at different temperatures were plotted to give a vapor pressure curve. A slight tendency for GeS to dissociate was noted. This tendency increased rapidly at temperatures of 600°C and higher.

Typical results of an extrapolation plot are shown in Fig. 1.

Table I. Analyses of Synthesized Germanium Sulfides

Material	Analysis, Pct		
	Ge	S	Total
Synthesized disulfide	51.1	48.1	99.2
Theoretical disulfide	53.1	46.9	100.0
Synthesized monosulfide	71.9	28.4	100.3
Theoretical monosulfide	69.4	30.6	100.0

Table II. Vapor Pressure Vs Temperature, GeS

Temperature, °C	Vapor Pressure Determined, Mm Hg	Vapor Pressure from Curve, Mm Hg
400	0.251	0.236
450	1.604	1.262
500	3.481	4.849
550	14.212	13.528
600	40.964	39.444

Table III. Temperature at Even Decimal Pressures for GeS

Pressure in Mm Hg	Temperature, °C
10^{-6}	317
10^{-5}	375
10^{-4}	447
10^{-3}	536
10^{-2}	650*

* The latter value may not be reliable since this is near the reported melting point of GeS (625°C).

Grade A helium, employed as the inert gas, was purified by passing it over heated black CuO, then through soda, lime, and activated alumina at room temperature. The furnacing apparatus included a fused silica tube in which an Alundum boat containing the GeS sample was placed, a smaller fused silica tube through which the hot gases immediately over the boat were withdrawn, and a manometer to indicate the pressure within the system. Discharged helium was collected and measured over helium-saturated water. Corrections were made for barometric pressure and room temperature. Temperatures of the GeS sample were determined by a Pt—Pt-13 pct Rh thermocouple placed over the charge.

Table IV. Apparent Vapor Pressures of GeS

Temperature, °C	Weight Loss, G per Cm^2 per Sec	Vapor Pressure, Mm Hg Determined	Vapor Pressure, Mm Hg from Curve
425	1.16×10^{-7}	5.50×10^{-6}	1.01×10^{-5}
450	7.86×10^{-7}	3.79×10^{-5}	3.71×10^{-5}
475	2.55×10^{-6}	1.25×10^{-4}	1.08×10^{-4}
500	1.19×10^{-5}	5.94×10^{-4}	3.91×10^{-4}
525	2.02×10^{-5}	1.02×10^{-3}	1.10×10^{-3}
550	3.71×10^{-5}	1.91×10^{-3}	2.50×10^{-3}

The equation $P = \frac{g}{MV} RT$ from Daniels[3] was used to calculate vapor pressures. In the equation P is the partial pressure in atmospheres due to the GeS, V is the volume which contains g grams of the vaporized monosulfide, M is the molecular weight of the gasified material, T is the absolute temperature, and R is the gas constant.

Calculated vapor pressures from 400° to 600°C are shown in Table II. The log of these values was plotted against $1000/T$, as illustrated in Fig. 2. Table II shows corresponding temperature values taken from the curve, which has been adjusted to the plotted points by the least squares method.

Values for P and T from the curve were sub-

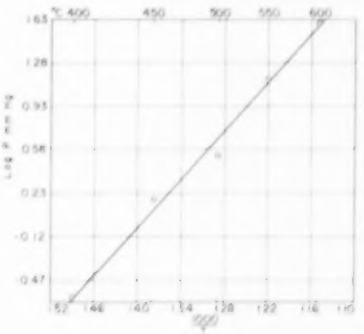

Fig. 2—Graph plots vapor pressure-temperature curve for GeS.

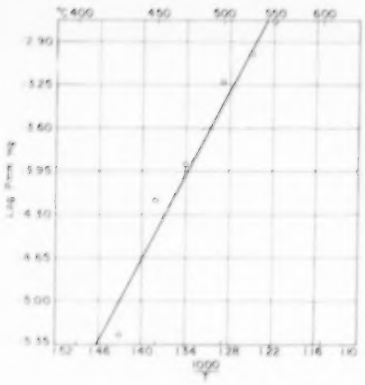

Fig. 3—Graph plots apparent vapor pressure-temperature curve for GeS_2.

stituted in the equation $\log P = \frac{-A}{T} + B$.[4] Simultaneous solutions gave values of 6526 for A and 9.07 for B. By substitution, the pressures tabulated in Table III were determined.

Apparent Vapor Pressure of GeS_2—GeS_2 is an unstable compound unless enveloped in a protective medium. It decomposes in moist air at room temperature and, in an inert gas at elevated temperatures, dissociation takes place, chiefly to sulfur and the monosulfide. In the following portions of this report the term *apparent vapor pressure* is used to indicate the total pressure of the dissociation products, which include GeS, S, and probably a limited amount of S_2. From observations and conclusions of others,[5] GeS_2 does not volatilize as such but dissociates to GeS and sulfur, which, upon cooling, partially recombine to give a mixture approximating Ge_2S_3 in over-all composition.

Table V. Temperatures at Even Decimal Pressures for GeS_2

Pressure in Mm Hg	Temperature, °C
10^{-1}	722
10^{-2}	626
10^{-3}	547
10^{-4}	481
10^{-5}	424
10^{-6}	376

The apparent vapor pressure of synthesized GeS, was determined by a procedure similar to that used by Hsiao and Schlechten.[6] Determination became erratic at 600°C because of rapid evaporation. At 400°C, evaporation was so slow that consistent results were not obtained, but conditions at 425° were sufficiently stable to give consistent results. Although the point shown at 425° deviates considerably from a curve constructed neglecting this point, the location of this point was made by numerous consistent determinations. Six samples were heated at one time in a vacuum of 5 to 10 μ. Loss in sample weights was considered the amount evaporated.

Vapor pressures were calculated from Langmuir's equation for vacuum conditions; $W = 5.883 \times 10^{-4} P \text{ mm } \sqrt{M/T}$ where W is the rate of gas evolution in g per sq cm per sec, P is the vapor pressure of the gas in mm of mercury, M is the molecular weight of the gas in g, and T is the absolute temperature.

The gaseous phase of the material was assumed to be 2 GeS and S_2; the average of the molecular weights was substituted for M. Calculations for P at selected temperatures gave the results shown in Table IV.

From these values, the curve in Fig. 3 was constructed.

A and B were determined as previously described.

Table VI. Analysis of Minerva Oil Co. Zinc Concentrate in Pct

Ge	Cd	Zn	Pb	S
0.024	0.89	63.0	0.027	30.7

Values obtained were: $A = 9330.86$, and $B = 8.37$. Substitution in the equation $\log P = \frac{-A}{T} + B$ gave the figures tabulated in Table V.

Pyrometallurgical Recovery from Zinc Concentrates

Analytical Studies—Petrographic examination of the Minerva Oil Co. zinc flotation concentrates showed that the sample consisted chiefly of sphalerite; with small amounts of calcite, fluorite, and silica; and a minute quantity of galena. Selected grains of sphalerite gave positive tests for cadmium and germanium. No primary minerals of cadmium or germanium were identified. Apparently these elements occurred in solid solution within the zinc mineral. Partial chemical analysis showed the concentrate to contain percentages of elements as listed in Table VI.

Table VII. Selected Volatilization Data

Material	Temperature, °C	Change of State
Germanium monosulfide	+430	Sublimed
Sulfur	445	Boiling Point
Germanium disulfide	+600	Sublimed
Germanium monoxide	710	Sublimed
Cadmium	767	Boiling Point
Zinc	907	Boiling Point
Cadmium sulfide	980	Sublimed
Zinc sulfide	1185	Sublimed
Lead sulfide	1280	Boiling Point
Lead	1613	Boiling Point
Germanium	(2700)	Boiling Point

Table VIII. Rougher Volatilization

Product	Weight, Pct	Analysis, Pct				Distribution, Pct			
		Ge	Cd	Zn	S	Ge	Cd	Zn	S
Rougher condensate	2.36	0.93	32.7	30.6	17.1	97.0	94.1	1.2	1.3
Primary residue	97.64	0.0007	0.05	62.9	30.9	3.0	5.9	98.8	98.7
Composite	100.00	0.023	0.82	62.1	30.6	100.0	100.0	100.0	100.0

Table IX. Upgrading Rougher Condensate

Product	Weight, Pct	Analysis, Pct				Distribution, Pct			
		Ge	Cd	Zn	S	Ge	Cd	Zn	S
Upgraded condensate	13.7	3.87	16.7	0.41	62.7	96.2	8.0	0.2	28.3
Upgrading residue	86.3	0.024	30.6	31.7	25.2	3.8	92.0	99.8	71.7
Composite	100.0	0.55	28.7	27.4	30.3	100.0	100.0	100.0	100.0

Extractive Studies—Numerous experiments were made to develop a method which would give consistent results for fuming cadmium, germanium, and lead from ZnS concentrates in an inert atmosphere. Tube furnaces were used exclusively for treating concentrates batchwise. The inert atmosphere consisted of helium, which was introduced at one end of the tube and discharged from the opposite end. Several methods of fume collection were tried, including cyclone, condensing chambers, bubbling through water, glass wool filtration, laboratory-size Cottrell, and condensing baffles. A combination of baffles and condensing chambers was favored for laboratory convenience. Fume recovery was in no instance as high as desirable. However, the system recovered a portion of fume which should closely characterize the whole.

Rougher Volatilization—Objectives of the research were to: 1) obtain a Ge-Cd impoverished residue, 2) remove over 90 pct of the germanium and cadmium, 3) vaporize a minimum of zinc, 4) determine the optimum temperature and time of treatment, and 5) consume only a small quantity of helium.

Table VII shows data pertinent to the studies. These are taken from chemical handbooks.

These figures indicate that it should be possible to distill sulfides of germanium and cadmium from the concentrates selectively, or to condense them from the fumes selectively while cooling. Several experiments were conducted along these lines, but overlapping characteristics and difficulties in separating the deposited fumes prevented any satisfactory degree of success.

For the production of a bulk fume or condensate, charges of approximately 1000 g Zn concentrate were placed in fused silica tubes and heated for 4 hr at 1090°C, while 4 l He per min were passed through the apparatus. Table VIII tabulates the results of a typical experiment.

The small amount of fluorspar in the feed caused extraneous volatile material to be present in the rougher condensate. In addition, some organic matter was present from volatilization of flotation reagents. The small amount of galena in the feed reported in the condensate also.

A revolatilization treatment of the rougher condensate at about 900°C was expected to produce a relatively high germanium fume and a second residue containing most of the zinc and cadmium. Contrary to expectation, most of the cadmium was volatilized, and the germanium and zinc were split between secondary fume and residue. This was due to a degree of dissociation of the sulfides, resulting in considerable metallic zinc and cadmium, and possibly metallic germanium. Addition of 20 pct S preceding upgrading or revolatilization produced quite different results. Zinc and cadmium were, to a great extent, retained in the residue, while the major portion of the germanium was reported in the upgraded fume, as shown in Table IX.

In several experiments the cadmium content of the condensate ranged from 6 to 10 pct. The amount of cadmium volatilizing can be loosely controlled by the quantity of sulfur added. The above results indicate that a few more percent of sulfur would have enhanced this particular separation. The composite does not check the rougher condensate. This is caused in part by dilution with sulfur and in part by fume losses, especially of germanium.

Desulfurizing Upgraded Fume—The upgraded condensate contained a large amount of sulfur—much of it in the elemental state. It was possible to remove this sulfur by CS_2 leaching, oxidation, or evaporation at relatively low or high temperatures. Recovery in a reuseable form was desired. Oxidation of the sulfur by heating or evaporation by boiling lost excessive quantities of germanium to the atmosphere. Volatilization by a prolonged low temperature treatment in air was found most suitable. By treating the upgraded condensate at an average temperature of 150°C for 35 hr, 87 pct of the sulfur was removed and probably could be condensed for reuse. Some germanium and a small amount of cadmium were also volatilized. However, this was not considered as a loss, since the sulfur returned to the circuit should contain nearly all of these elements. The final product analyzed 7.03 pct Ge, 35.2 pct Cd, 26.2 pct S, and 0.77 pct Zn. Over-all recovery, based on residues, was 94.9 pct of the germanium and 87.2 pct of the cadmium. The cadmium in the germanium condensate represented an additional 7.5 pct of the cadmium present in the original zinc concentrate. This could largely be recovered in a hydrometallurgical separation scheme when the germanium is recovered, thus raising cadmium recovery to more than 90 pct.

Summary

The fuming experiments have shown that germanium and cadmium may be removed effectively by heating certain sphalerite concentrates in an inert atmosphere. The ratios of concentration are high, approximating 300:1 for germanium and 35:1 for cadmium. The final pyrometallurgical products were of sufficient tenor to be treated by hydrometallurgical methods to obtain finished products.

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Diffusion of Nitrogen in Iron

The diffusion of nitrogen in α-iron was studied by means of the fractional saturation method. Resulting diffusion coefficients are in excellent agreement with the values obtained from internal friction experiments.

by Paul E. Busby, Donald P. Hart, and Cyril Wells

EARLY workers in the field have established that the diffusion of nitrogen follows normal diffusion laws. Concentration-penetration data from layer analyses of reasonably pure iron specimens nitrided in an atmosphere of CO-NH_3 are given in the literature,[1] and were utilized to calculate diffusion constants for nitrogen. The diffusion of nitrogen in γ-iron may be represented approximately by the equation

$$D = 1.07 \times 10^{-1} e^{-24,\,100/RT}.$$

The diffusion coefficients, D, given by this relation represent mean values, since carburization occurred simultaneously with nitriding.

The rate of diffusion in α-iron has been determined from calculations based on data obtained by measuring the internal friction of samples at each of several frequencies and temperatures.[2] The expression for the diffusion of nitrogen in α-iron derived from these experiments is

$$D = 1.4 \times 10^{-4} e^{-17,\,700/RT}.$$

Increasing carbon content decreases the diffusion of nitrogen in α-iron.[3] Oxygen, either dissolved or combined, has been shown[4] to exert a marked influence on the diffusion of nitrogen from a nitriding atmosphere. D values increase rapidly with increasing amount of dissolved oxide in the metal, but diffusion is completely inhibited if preliminary oxidation has produced the slightest trace of iron oxide on the surface. Diffusion coefficients have also been calculated from permeability and solubility data,[5] but these values are of questionable accuracy since the boundary conditions assumed may not actually exist.

Experimental Method

The method selected for determining the diffusion coefficient of nitrogen in α-iron in the present investigation was the so-called fractional saturation method. This method consists of heating the specimen in an atmosphere of H_2-NH_3 mixtures of known composition for a predetermined time. Following this treatment, the specimen is analyzed for nitrogen; and the diffusion coefficient is calculated from a known relationship of the fractional saturation, time of diffusion, and dimensions of the specimen.

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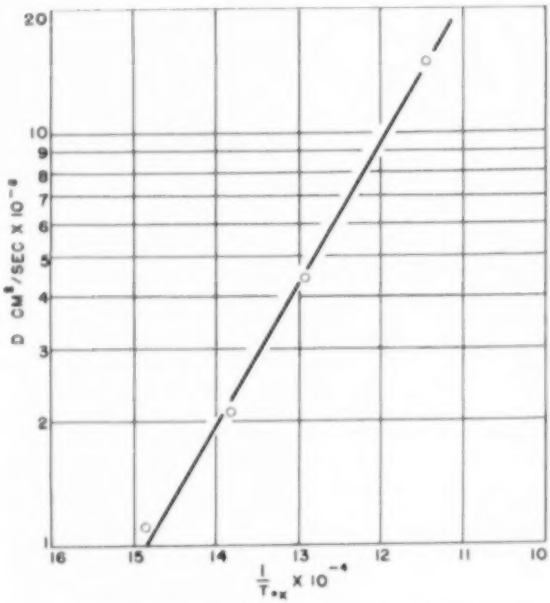

Fig. 1—Graph plots effect of temperature on the diffusion coefficient for nitrogen in α-iron.

This relation is based on a solution of Fick's second law and assumes that the surface of the specimen immediately reaches a given concentration which remains constant during the diffusion anneal. Tabular solutions are available[6-8] and provide the relationship between fractional saturation and the quantity $\sqrt{Dt}/a$, where D is the diffusion coefficient in cm² per sec, t is the time of the diffusion anneal in seconds, and a, in the present experiments, is the half-thickness of the slab specimen in cm. The method is adequately discussed elsewhere.[9, 10]

Material

The material for this study consisted of 3/32 in. thick (0.24 cm) carbonyl iron plate. The major impurities in this iron are oxygen and carbon, which are readily removed by long time high temperature treatment in an atmosphere of purified hydrogen. In order to reduce the diffusion anneal time for saturation runs, some of this material was rolled to a thickness of 0.015 in. (0.038 cm) prior to the hydrogen treatment.

Hydrogen treatments were carried out in a hydrogen-purified Armco iron tube heated in a globar

furnace. The carbonyl iron samples, cut into strips about 2 in. wide and 8 in. long, were supported on a previously purified carbonyl iron holder in a position which exposed a maximum of surface to the hydrogen atmosphere. The gas was passed through pyrogallic acid, H_2SO_4, and Drierite, respectively, prior to admission to the charge. For the duration of the one month purification treatment, the flow rate of hydrogen was about 4 cu ft per day and the furnace temperature was maintained at 1200°C. A typical analysis of the purified iron is as follows: Carbon, not determined, <0.005 Mn, 0.005 P, 0.0001 S, 0.002 Si, <0.007 Ni, <0.001 Cr, <0.005 Mo, 0.001 Cu, <0.001 Al, <0.001 Sn, 0.002 O_2, 0.0005 H_2, and 0.0009 N_2.

Gas Mixer

The NH_3-H_2 atmosphere for the diffusion experiments was provided by a gas-mixing apparatus constructed for the purpose. The apparatus is a modification of that described by Johnston and Walker[11] and later modified by Darken and Gurry.[12] In brief, the assembly permits close control of the flow rates (0 to 100 cu cm per min for NH_3 and 0 to 150 cu cm per min for H_2) required to provide the desired compositions and flow rates of the gas mixtures for the furnace atmosphere. Chemical analyses of the gas mixtures were carried out by obtaining a sample of the mixture in a flask of known volume at ambient temperature and pressure, introducing a known amount of standard H_2SO_4, and back-titrating the excess acid with standard alkali so that the percentage of ammonia could be calculated from the amount of acid neutralized.

Diffusion Anneal

Specimens of the purified iron about 2 in. sq were subjected to treatments in NH_3-H_2 mixtures at temperatures ranging from 400° to 600°C. The heating unit consisted of a wire wound Alundum tube furnace controlled within ±1°C of the desired temperature by a Micromax controller. An inner liner of Pyrex 172, which is satisfactory for continued use at temperatures below 675°C, served as the atmosphere chamber. Specimens to be annealed were charged into the cold furnace and heated to the desired temperature in hydrogen only. After thermal equilibrium was attained, the ammonia was introduced to provide a previously determined mixture. During the diffusion period, the analysis of the gas entering and leaving the furnace was checked periodically by drawing off a sample of it for chemical analysis. The flow rate of approximately 100 cu cm per min was found to be sufficient to prevent change of the composition of the gas during passage through the furnace. After the annealing treatment, specimens were removed from the furnace and quenched in water. The time for the diffusion anneal was considered to be the elapsed time from the introduction of the ammonia to the water quench.

Choice of the NH_3-H_2 mixture was based on results given by Lehrer,[13] whose data suggest that specimens heated at temperatures of 450°C in 27 pct NH_3, 500°C in 21 pct NH_3, and 600°C in 10.5 pct NH_3 should contain, at temperature, all the nitrogen in α solid solution. Actually, specimens heated at 500°C in mixtures containing 20 pct NH_3 were observed microscopically to contain nitrides which probably formed at the diffusion temperature. X-ray analyses indicated that these nitrides were Fe_4N. In later experiments, therefore, the compositions of the mixtures were arbitrarily reduced to values of about 20, 15, and 9 pct NH_3 at 400°, 500°, and 600°C, respectively, to insure against the formation of nitrides.

Following the diffusion anneal, specimens were analyzed for nitrogen by standard chemical techniques. In order to satisfy the conditions of a semi-infinite solid, the outer portions of the 3/32 in. thick specimens were discarded and only the center ½ in. sq section of the specimen was analyzed for nitrogen. No discard was made on the sheet specimens which were saturated with nitrogen.

Table I. Summary of Diffusion Treatments

Test No.	Specimen No.	Temperature, °C	Time, Hr	NH_3, Pct	N_2, Pct	$Dx10^6$ Cm^2 per Sec
1	N-30	400	30.6	20	0.029	*
2	N-26	400	19.0	20	0.008	1.1
3	N-29	450	30.6	20	0.038	*
4	N-25	450	19.0	20	0.014	2.1
5	N-19	500	21.1	15	0.014	*
6	N-20	500	21.1	15	0.008	4.4
7	N-11	600	6.3	9	0.087	*
8	N-13	600	16.0	9	0.071	14.8

* Saturation run.

Results

A summary of the data is given in Table I, which lists the time and temperature of the diffusion heat treatments as well as the D values calculated from the resulting nitrogen analyses. The value of the activation energy, Q, determined from the line of best fit on the plot of log D vs $1/T$, Fig. 1, is 15,600 cal per mol, so that the diffusion of nitrogen in α-iron is represented by the relation

$$D = 1.2 \times 10^{-4} e^{-15,600/RT}$$

as compared with the equation

$$D = 1.4 \times 10^{-4} e^{-17,700/RT}$$

determined from internal friction measurements.[9]

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Purification of $GeCl_4$ by Extraction With HCl and Chlorine

$GeCl_4$ may be purified by extraction with HCl and chlorine. The process is as effective for the removal of $AsCl_3$ as the more cumbersome distillation methods usually used for this purpose.

by H. C. Theuerer

GERMANIUM for semiconductor use contains impurities at levels no higher than a few parts in ten million. Material of this quality is obtained from highly purified $GeCl_4$ by hydrolysis to the oxide and reduction of the oxide in hydrogen. When purifying $GeCl_4$, $AsCl_3$ is the most difficult impurity to remove. This is usually accomplished by multiple distillation procedures.[1-3]

$AsCl_3$ may also be removed from $GeCl_4$ by extraction with HCl.[4-6] Reducing the arsenic to low concentrations is not practicable, however, because of the large number of extractions needed. This paper discusses a new method for the removal of arsenic from $GeCl_4$ by extraction with HCl and chlorine. The method is rapid, leads to little loss of germanium and is at least as efficient as the distillation procedures currently being used.

Theory of Extraction Procedures

In the simple extraction of $GeCl_4$ with HCl, the following reaction occurs

$$AsCl_{3_{GeCl_4}} \rightleftarrows AsCl_{3_{HCl}}$$

at equilibrium $C_A/C_B = K$, where K is the distribution coefficient, and C_A and C_B are the molar concentrations of $AsCl_3$ in HCl and $GeCl_4$, respectively.

The materials balance equation for this reaction is

$$V_A C_A + V_B C_B = V_B C_o$$

where V_A and V_B are the volumes of HCl and $GeCl_4$, respectively, and C_o is the initial concentration of $AsCl_3$ in $GeCl_4$. From this it can be shown that for multiple extractions

$$\frac{C_n}{C_o} = \left(\frac{1}{Kr+1}\right)^n \qquad [1]$$

where C_n is the concentration of $AsCl_3$ in $GeCl_4$ after n extractions, and r is the ratio of V_A to V_B. It is assumed that r is maintained constant, that equilibrium is established during each extraction, and that K is independent of the $AsCl_3$ concentration.

By saturating the system with chlorine, the following reaction occurs in the aqueous phase

$$AsCl_3 + 4H_2O + Cl_2 \rightleftarrows H_3AsO_4 + 5HCl$$

at equilibrium

$$K' = \frac{a_{H_3AsO_4} \cdot a^5_{HCl}}{a_{AsCl_3} \cdot a^4_{H_2O} \cdot a_{Cl_2}}$$

where a is the activity of the various components. The effect of this reaction is to reduce the concentration of the $AsCl_3$ in the aqueous layer and, therefore, to promote further extraction of this component from the $GeCl_4$ layer. If the arsenic acid remains entirely in the aqueous phase, the net effect of this reaction is to promote the removal of arsenic from the $GeCl_4$. The materials balance equation for extraction with HCl and chlorine with the foregoing reaction is, then,

$$V_A C_c + V_A C_A + V_B C_B = V_B C_o$$

where C_c is the molar concentration of H_3AsO_4 in the HCl. With the added assumptions that the activities of $AsCl_3$ and H_3AsO_4 in the aqueous phase are equal to their molar concentrations, it can be shown that for n extractions

$$\frac{C_n}{C_o} = \left(\frac{1}{rkK + rK + 1}\right)^n \qquad [2]$$

where

$$k = K' \frac{a^4_{H_2O} \cdot a_{Cl_2}}{a^5_{HCl}}.$$

It can be seen by comparing Eqs. 1 and 2 that if k is large, the removal of $AsCl_3$ by HCl extraction will be greatly improved by the addition of chlorine. Dilution of the HCl used in the extraction with chlorine would also favor the separation. This, however, would increase the loss of $GeCl_4$, which is undesirable.

Experimental Procedure

Germanium prepared from oxide of semiconductor purity is n-type with resistivities greater than one ohm-cm. The resistivity is controlled by the donor concentration, which is $\sim 10^{-5}$ mol pct. Germanium prepared from material with added arsenic will have lower resistivity commensurate with the arsenic concentration. With such material, at arsenic concentrations above 10^{-4} mol pct the resistivity is controlled by the added arsenic, and effects due to other impurities initially in the oxide are negligible. In this investigation GeO_2 of semiconductor purity was converted to $GeCl_4$, and ~0.01 mol pct As was added. This material was used for the extraction experiments and the purification attained determined by a comparison of the resistivity data for samples of germanium prepared from the initial and purified $GeCl_4$. A method for calculating the arsenic concentration from the resistivity data is discussed later. The details of the experimental procedures used are as follows:

Two hundred and thirty cu cm $GeCl_4$ were prepared by the solution of GeO_2 in HCl, followed by

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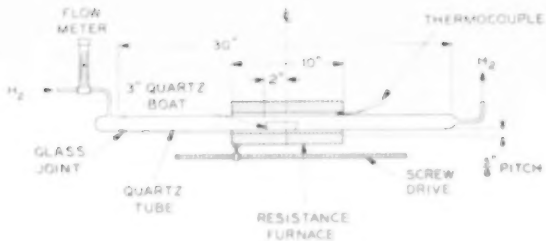

Fig. 1—Apparatus for the reduction of GeO_2 is illustrated.

distillation. To the distilled $GeCl_4$, 0.0278 g As_2O_3 dissolved in 50 cu cm HCl was added. This mixture was agitated vigorously and allowed to stand several days. The two layers were then separated and the GeCl, divided into two 100 cu cm portions and one 25 cu cm portion, which was held as a control. The two 100 cu cm portions were used in parallel extraction experiments using, in one case, HCl, and in the other, HCl and chlorine. One portion was given two extractions with 50 cu cm HCl (37.4 pct) using fresh acid for each extraction. The second 100 cu cm portion was extracted twice under conditions identical to the foregoing, except that both the HCl and GeCl, were saturated with chlorine.

During each extraction the samples were kept chilled in an ice bath and were agitated vigorously at intervals during a 45 min period. Separations between extractions were made with a separatory funnel. After the second extraction, 25 cu cm samples of the GeCl, were removed from each portion and the remaining portions given two additional extractions, following the same procedure as before. After the fourth extraction, 25 cu cm samples were again withdrawn. As a final experiment, 50 cu cm of the GeCl, which had been extracted four times with HCl alone were extracted with 36 cu cm HCl with the system saturated with chlorine. The extraction was carried out as before and a 25 cu cm sample separated.

Each of the six 25 cu cm samples was separately hydrolyzed in six volumes of doubly distilled water, washed and dried. Fifteen g samples of the resultant oxide were then hydrogen-reduced at 650°C in quartz boats, using the equipment shown in Fig. 1. After reduction, the germanium was melted at 1000°C, and a normally solidified ingot produced by withdrawing the boat from the furnace at the rate of 3/32 in. per min. This resulted in ingots approximately 1⅜ in. long and ¼ in. in cross section. Rectangular bars were cut lengthwise from the ingots and resistivity measurements made along the bar. From such resistivity measurements it is possible to calculate the arsenic concentration in the germanium using the following relationship[7]

$$C = \frac{1}{\rho e m}$$

where C = the concentration of arsenic in atoms per cu cm of germanium, e = the charge on the electron in coulombs, ρ = the resistivity in ohm-cm, and m = the mobility in $cm^2\ volt^{-1}\ sec^{-1}$.

Values for the mobility of electrons in n-type germanium have been determined,[8] making it possible to evaluate the concentration C when the resistivity is known. Since the experimental ingots were normally solidified, the arsenic concentration and therefore the resistivity varies as a function of ingot location in accordance with the following equation[9]

$$C_x = C_0 (1 - x)^{k-1}$$

where k = the distribution coefficient for arsenic in germanium, C_x = the concentration of arsenic at a given location in the bar, C_0 = the initial concentration of arsenic in germanium, and x = the distance from lead end/total length.

Since values for C_x may be determined from the resistivity data, if the distribution coefficient for arsenic in germanium is known, the initial concentration of arsenic, C_0, may be calculated. The value of the distribution coefficient using radioactive tracer methods[10] has been found to be 0.06. Fig. 2 gives plots of resistivity as a function of rod location for representative samples. Included for comparison is a typical plot for material prepared by the conventional distillation procedures. In Table I the median resistivity obtained with each of the samples, the corresponding concentrations of arsenic in the germanium, and the fraction of arsenic remaining after the various extractions are given. From these data the values for the constants in the theoretical extraction equations may be determined.

Table I. Extraction of GeCl, with HCl Solutions

No. of Extractions	Extraction Solution	ρ, Ohm-Cm	Atoms As / Cm^3 Ge	C_x/C_0
0	—	0.011	3.5×10^{19}	—
2	HCl	0.016	1.9×10^{19}	0.54
4	HCl	0.023	1.2×10^{19}	0.34
4	HCl	3.1	5.3×10^{15}	0.0044
1	HCl + Cl_2			
2	HCl + Cl_2	2.1	8.3×10^{15}	0.0024
4	HCl + Cl_2	2.8	6.1×10^{15}	0.0017

Discussion of Results

From the curves of Fig. 2 and the data in Table I, it is at once apparent that extraction with HCl and chlorine is much more effective for the removal of AsCl, from GeCl, than HCl extraction alone. After

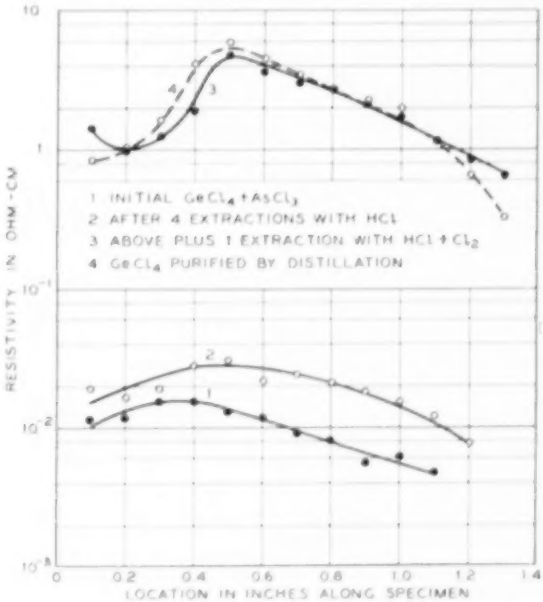

Fig. 2—Purification of GeCl, by extractive procedures is plotted.

four extractions with HCl, 34 pct of the $AsCl_3$ remained in the $GeCl_4$, whereas with one subsequent extraction with HCl and chlorine alone, 0.44 pct remained. With two extractions using HCl and chlorine, 0.24 pct of the $AsCl_3$ remained, and further purification to 0.17 pct resulted with four extractions. Germanium of this quality is as good as material prepared by the multiple distillation process for the purification of the tetrachloride, as shown in Fig. 2.

With the data for the extractions with HCl, values of the distribution coefficient for the extraction process were calculated, using Eq. 1. Values from 0.75 to 0.40 were obtained, the values being smaller for smaller $AsCl_3$ concentrations. From these data it would appear that at low concentrations the effective distribution coefficient and, therefore, the efficiency of the extraction process, diminishes. Using an average distribution coefficient, K, of 0.58, and the data for a single extraction with HCl and chlorine, the value of k in Eq. 2 was estimated to be 5.3×10^{7}. With this value, the second and fourth extractions should have reduced the arsenic concentration to values of 1.4×10^{14} and 3.3×10^{9} atoms per cm^3, respectively. Actually, multiple extractions, as seen in Table I, resulted in only minor reductions in arsenic concentration. The reason for this has not been established.

If, as has been suggested, the distribution coefficient, K, diminishes as a function of the $AsCl_3$ concentration, then it can be seen from Eq. 2 that further separation would be impossible as K approached zero. The apparent termination of arsenic extraction at levels corresponding to 5×10^{15} atoms per cm^3 of germanium may, however, be inherent in the experimental procedures used. It is entirely possible that contamination to the above level with arsenic or other group V impurities is introduced during the hydrolysis and reduction processes. In support of this viewpoint, experience with the reduction process used in this work has indicated that regardless of the source of the oxide or its preparation, the lower level of donor impurities is of the order of 10^{15} atoms per cm^3 of germanium.

Summary

It has been shown that $AsCl_3$ can be removed from $GeCl_4$ by extraction with HCl and chlorine. Germanium prepared from this purified tetrachloride contains 5×10^{15} atoms per cm^3 of arsenic, which is as good as that obtained by the more difficult distillation procedures. The extraction method is simple and readily adaptable to the quantity production of GeO_2, either from primary crude oxide or from germanium scrap material. The extraction procedure may be used in a batch process with two or more extraction stages. To minimize loss of $GeCl_4$, the HCl from each stage may be used in the preceding stage of a subsequent batch, the impure acid from the first stage being used to convert the crude oxide to the tetrachloride for the extraction process. Alternatively, the process could be adapted to continuous extraction methods in which countercurrent flow of $GeCl_4$ and Cl_2-HCl solution is maintained.

Acknowledgment

The author is indebted to J. H. Scaff for many valuable discussions and much encouragement.

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Direct Measurement of Ferrous Ion Mobility in Liquid Iron Silicate by a Radioactive Tracer Technique

A method is described for using radioactive tracer for the direct determination of ionic mobility in a molten electrolyte. The ionic mobility of Fe^{++} in silica-saturated iron silicate is found to be 0.0009 ($\pm$0.0002) $cm^2\ sec^{-1}\ volt^{-1}$ at 1250°C.

by M. T. Simnad, Ling Yang, and G. Derge

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TP 4197CD. Manuscript, Oct. 15, 1954.

ELECTROCHEMICAL studies[1-9] of molten iron oxide and iron silicates have shown some ionic conductivity at all compositions. The current efficiency in electrolysis increases with the concentration of silica to a maximum of 90 pct at about 34 pct SiO_2. In the silica-saturated melts the transport number of ferrous ions is near unity, indicating that

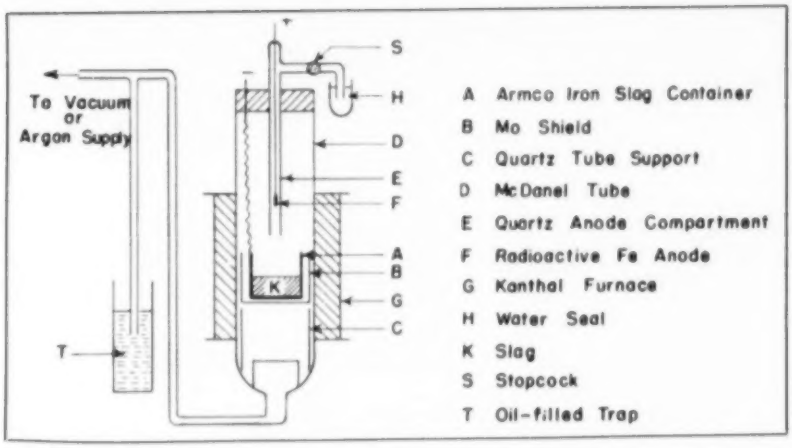

Fig. 1—Diagram shows schematic arrangement for the direct measurement of ionic mobility by radioactive tracer techniques.

these cations carry all of the ionic current. In this paper, the measurement of ferrous ion mobility is described.

The most direct approach is to use radioactive iron as tracer and observe the distance traveled by the cation under a known potential gradient in a given time. The mobility is then calculated by the equation

$$\mu = \frac{dL}{tE}$$

where d is the distance in cm traveled by the ion in t sec and E is the potential in volts applied across the electrodes separated by L cm.

The apparatus, shown schematically in Fig. 1, is similar to that described for transport studies.[4] The slag container, *A*, which also served as the cathode, was an ingot iron crucible. It was 4 in. deep, and had a wall thickness of 1/16 in. and an ID of ⅞ in. Surrounding the crucible was a molybdenum shield, *B*. Both the shield and the crucible rested on a silica tube, *C*, which fitted closely inside a McDanel tube, *D*, 48 in. long, with a 1½ in. ID. The anode compartment consisted of a silica tube, *E*, of ¼ in. ID, which could be pushed into the slag in the iron crucible or withdrawn from it through a gas-tight seal at the top of the McDanel tube. The anode, *F*, was a cylindrical piece of ingot iron ⅛ in. diam and 1½ in. long. It was welded to the end of an iron wire and inserted into the anode compartment so that the lower tip of the anode was about 6 in. above the lower end of the silica tube, *E*. Before electrolysis, radioactive Fe^{55-59} was plated on the lower end of the anode for a length of about ⅜ in. from a sulfate bath at 70°C and 0.1 amp per cm², with an iron wire as anode. The plating was continued until the electrode showed an activity of about 2,000 counts per min. Usually about 0.3 g Fe was deposited before such an activity was reached.

The measurement of mobility was carried out as follows. Enough prefused silica-saturated iron silicate slag was added to the iron crucible to give a slag depth of about 1½ in. after melting. The whole system was assembled and put inside a Kanthal resistance tube furnace, *G*. The winding of the furnace was such that the bottom of the iron crucible was about 5° cooler than the top in order to minimize stirring by convection. A control Pt—Pt-Rh thermocouple attached to the furnace tube indicated the temperature of the latter, from which the temperature of the crucible could be deduced by means of a calibration curve. The system was evacuated and flushed with argon, and the slag then homogenized at 1250°C for 2 hr. The arrival of the lower end of the anode compartment at the surface of the liquid slag was indicated by the disappearance of argon gas bubbles at the water seal, *H*, connected to the top of the anode compartment and the appearance of argon gas bubbles at the oil-filled trap, *T*, connected to the bottom of the McDanel tube. The silica tube which served as the anode compartment was lowered into the liquid slag until the lower end touched the bottom of the iron crucible. Then the argon pressure inside the McDanel tube was increased by lowering the glass tube into the oil in *H* until the slag level inside the anode compartment was raised to a height of about 6 in. Contact of the slag with the radioactive iron anode was indicated by the ammeter connected in the electrolytic circuit.

Electrolysis was then continued at the predetermined current, voltage, and time. At the end of the electrolysis, the stopcock, *S*, connected to the top of the anode compartment was closed and the anode compartment, with the slag in it, was pulled out of the liquid slag to the colder region at the upper part of the McDanel tube. After the furnace was cooled, the anode compartment was taken out and the part containing the slag cut off. An autoradiograph was taken, using double immersion X-ray film and an exposure of about one week. A densitometer tracing was made, the distance the iron traveled during the electrolysis was measured, corrections applied and the mobility calculated.

The corrections were determined experimentally by blank runs in which the same procedure was followed without electrolysis. The difference between the densitometer tracings of the blank and the electrolysis runs would thus correct for:

1—Scatter of the radioactivity by slag, silica anode tube, air, and film. The radiations emitted

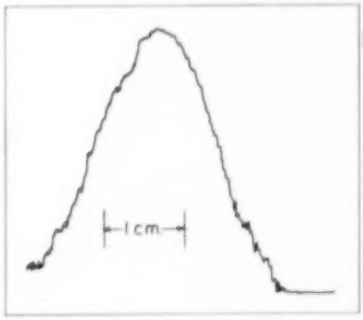

Fig. 2—Microdensitometer tracing of an autoradiograph of a blank run at 1250°C for 5 min is shown.

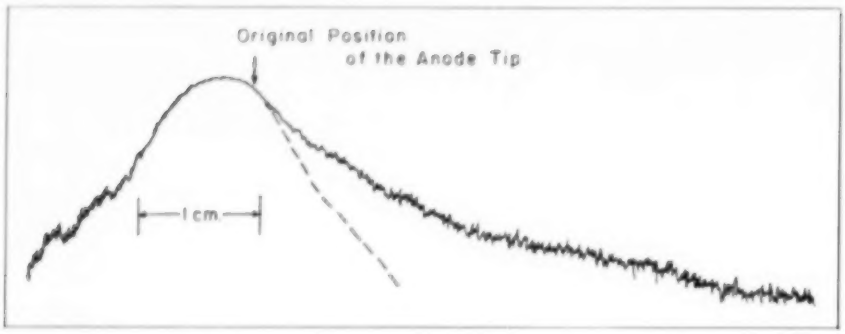

Fig. 3—Microdensitometer tracing of an autoradiograph of an electrolysis run at 1250°C for 30 min is shown. *E* equals 40 v; *L*, 15 cm.

from the radioactive anode, due to their penetrating power—Fe^{55} = *K* capture X-ray; Fe^{59} = β-ray, 0.26 and 0.46 mev; γ-ray, 1.1 and 1.3 mev—affect the photographic film even at a certain distance.

2—The activity resulting from the self-diffusion of Fe^{++} in the slag as a result of the exchange reaction

$$Fe^{*}_{anode} + Fe^{++}_{slag} \rightleftharpoons Fe_{anode} + Fe^{*++}_{slag}.$$

The quantitative mathematical analysis of these factors is the subject of a separate paper.[5]

Two runs will be described in which the experimental variables were combined so as to give satisfactory measurements. It is obvious that too little electrolysis will not give a significant difference from the blank; too much electrolysis will leave too weak an activity. The several runs required to establish these conditions are not reported. Electrolysis was at 1250°C. Fig. 2 is a microdensitometer tracing of an autoradiograph for a 5 min blank run. It can be seen that the activity was concentrated at the region around the radioactive anode tip and the symmetrical spread on each side is about 1.5 cm. Tracings for 30 min blank runs are similar to Fig. 2, and the spread of the activity from the central position is again about 1.5 cm. Therefore, there was no time dependent convection, and the spread of activity due to the other factors mentioned did not extend beyond a distance of 1.5 cm under these experimental conditions.

Fig. 3 is the tracing from an autoradiograph taken from the anode compartment after an electrolysis at 0.9 amp, 40 v for 17 min. The dashed line is the reflection of the curve above the anode tip, where no electrolysis occurred, and is equivalent to the blank correction. The spread of activity due to the electrolytic migration of the Fe^{++} is evident. The Fe^{++} traveled 4.0 cm. Similarly, during an electrolysis at 1.2 amp, 50 v for 30 min, the Fe^{++} traveled 6.6 cm.

If the measured distances of 4.0 and 6.6 cm are corrected 1.5 cm, the mobilities of Fe^{++} at 1250°C in silica-saturated iron silicate slag can be calculated from the equation

$$\mu = \frac{dL}{tE}$$

with d = 2.5 and 5.1 cm, t = 1020 and 1800 sec, E = 40 and 50 v, and L = 15 cm, giving μ = 0.00094 and 0.00085 cm^2/v sec, respectively. Average μ at 1250°C = 0.0009 ± 0.0002 cm^2/v sec.

It is interesting to use this value of mobility in the conventional calculation of the self-diffusion coefficient, *D*, by the Nernst-Einstein relation

$$\mu = \frac{Ze}{300\,kT}\,D$$

where Z = valence of the ion, 2 for Fe^{++}; e = the electronic charge, 4.80×10^{-10} electrostatic units; k = the Boltzman constant, 1.38×10^{-16} ergs per degree per mol; and T = the absolute temperature. This gives D for Fe^{++} at 1250°C = 5.8×10^{-5} cm^2 per sec.

It is also possible to make a formal calculation of the concentration of the conducting ions, *C*, through the relation

$$\sigma\,\tau = \mu CFZ$$

where σ = specific conductance = 1.1 ohm^{-1} cm^{-1};[5,6] τ = proportion of current carried by Fe^{++}, 0.9;[7] μ = mobility of conducting ion, Fe^{++} = 0.0009 cm^2 per v sec; F = Faraday's constant, 96,500 coulombs per equivalent; and Z = valence of conducting ion, 2. This gives C = 0.0057 mol of Fe^{++} per cu cm conducting the current. The corresponding value of *C*, based on the analyzed slag composition (61 wt pct FeO, neglecting the small amount of Fe^{+++}), and taking the slag density as 4 g per cu cm,[8] is C = 0.034 mol of Fe^{++} per cu cm.

One interpretation of this is that at any given instant only 17 pct of the total iron in the slag is participating in ionic conduction. Further speculation as to the meaning of this result is beyond the scope of this paper.

Conclusion and Summary

These experiments with radioactive iron tracer have furnished direct evidence of the electrolytic migration of Fe^{++} in silica-saturated iron silicate and a measurement of the mobility of Fe^{++} at 1250°C of μ = 0.0009 cm^2 per v sec.

Acknowledgments

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Sulfur Pressure Measurements Above FeS In Equilibrium With Iron

Sulfur pressure measurements above FeS in equilibrium with iron have been carried out by the Knudsen orifice method. A comparison is made of the weight loss of the cell per unit time obtained in the above experiments, that calculated from Richardson and Alcock's measurements of the S_2 pressure above FeS in equilibrium with iron, and the dissociation constant for diatomic sulfur from spectroscopic and thermal data.

by C. L. McCabe, C. B. Alcock, and R. G. Hudson

EXTENSIVE equilibrium measurements have been made to determine the sulfur potentials of a great many systems of metallurgical interest.[1] In order to confirm their reliability, to supply data which may be of use in further thermodynamic calculations, and to establish the reliability of the Knudsen orifice in obtaining accurate thermodynamic values at high temperatures, the present investigation on the pressure of the gaseous species above FeS in equilibrium with iron has been carried out. The Knudsen orifice method has been used for these pressure measurements.

Experimental

The apparatus and general technique for this investigation are the same as that reported for the determination of the vapor pressure of silver.[2] To reduce the residual gas pressure in the evacuated chamber, a titanium getter, maintained at run temperature, was introduced. Several types of Knudsen cells were used—platinum, zircon, and fused silica. The orifice in the zircon cell was fashioned with a small diamond wheel.

The same precautions were used in this investigation as were employed in the work on Mo_2S_3.[3]

The FeS-Fe mixture was prepared by heating a sample of pure FeS, supplied by K. K. Kelley of the Bureau of Mines, with excess iron powder, cp grade, obtained from the Fisher Scientific Co. These two substances were heated in a closed Armco iron crucible at 960°C, held in a vacuum of less than 10^{-4} mm Hg for 24 hr. The mass was then removed from the cell and ground in an agate mortar. In this form it was charged to the various Knudsen cells. Heating the Knudsen cell for an additional two days was sufficient to obtain constant rates of weight loss of the cell. The data obtained in this investigation are recorded in Table I.

To establish whether or not a sulfide of iron is volatile at these temperatures, 0.7646 g of the FeS-Fe mixture, described above and containing 69.2 pct Fe, was placed in the zircon Knudsen cell. Run Nos. 103 to 109 were performed on it. After the completion of these runs, the total amount of iron left in the cell was obtained by chemical analysis. It contained 0.537 g Fe, compared to 0.529 g in the original charge. Thus, there was an apparent gain in iron of 1.5 pct. This is attributed to unknown experimental error, and the conclusion is that no sulfide of iron is volatile. The vapor pressure of pure iron[4] is about one thousandth that of the sulfur pressure[1] at these temperatures. The vapor pressure of iron inside the Knudsen cell will be almost exactly that of pure iron, since in the iron-rich phase the percentage of sulfur is of the order of 0.025 pct.[5] At this low percentage of sulfur Henry's law is probably obeyed by the sulfur. Thus, the iron will obey Raoult's law. In any event, the vapor pressure of iron will be lower than that of pure iron and, since the vapor pressure of pure iron is negligible compared to the pressure of sulfur, the weight loss of the cell due to the vaporization of iron should be negligible. Since neither iron nor FeS is volatile to an appreciable extent, the total weight loss of the cell must be due to the vaporization of sulfur.

Table I. Summary of Experimental Data

Run No.	Cell	a, Cm²	Duration of Run, Min	WL, G	$1/T \times 10^4$	P_{S_2}, Atm $\times 10^7$
115	Platinum	0.0260	11265	0.0126	8.143	0.709
116	Platinum	0.0260	6900	0.0079	8.143	0.726
47	Silica	0.0287	9967	0.0134	8.110	0.771
54	Silica	0.0287	6825	0.0121	8.032	1.02
103	Zircon	0.0315	9586	0.0146	8.097	0.801
104	Zircon	0.0315	9550	0.0146	8.097	0.795
105	Zircon	0.0315	6955	0.0077	8.170	0.596
106	Zircon	0.0315	6935	0.0118	8.032	0.900
108	Zircon	0.0315	6720	0.0155	7.968	1.21
109	Zircon	0.0315	6999	0.0092	8.117	0.686

Discussion and Calculations

On the assumption that S_2 is the only gaseous species present in appreciable quantity, its pressure

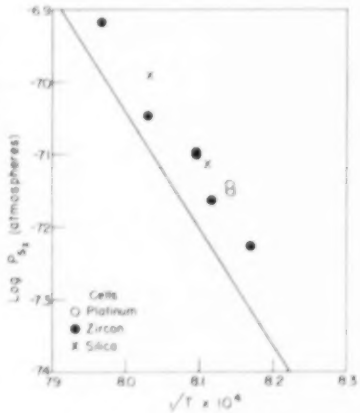

Fig. 1—Experimental values for log P_{S_2} are calculated from the Knudsen cell experimentals reported here, assuming that only S_2 is effusing, vs $1/T$. The solid line is P_{S_2}, calculated from the data of Richardson and Alcock.[1]

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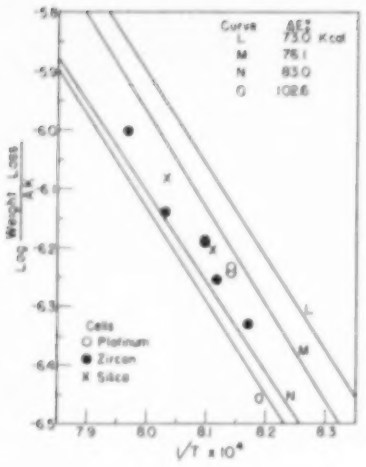

Fig. 2—Values for $(WL)/(A)(K)$ vs $1/T$ are obtained from the Knudsen cell experiments reported here, and those calculated from the gas equilibria data of Richardson and Alcock in conjunction with the equilibrium constant for the reaction $S_2 \leftrightarrows 2S$, assuming various suggested values for $\Delta E°_0$ for this reaction.

may be calculated from the data in Table I, using the ordinary Knudsen formula.[7] The calculated values are given in Table I and the values are graphed in Fig. 1. Also shown in Fig. 1 is the pressure of S_2, calculated from the gas equilibrium data of Richardson and Alcock.[1] It is obvious, if both sets of data are accurate, that some other species is present in the gas phase, and is effusing. The data are sufficiently accurate to assume that this discrepancy is due to the presence of monatomic sulfur.

Table II. Cell Data

Cell	W_A	f	K
Platinum	0.581	0.0100	0.993
Zircon	0.552	0.0121	0.989
Silica	0.526	0.0144	0.987

Data for the standard free energy of dissociation of diatomic sulfur going to monatomic sulfur have been compiled by Richardson and Jeffes.[1] Kelley[6] also has done extensive calculations on the standard free energy for this reaction from the spectroscopic energy of dissociation and thermal data. His calculations have been assumed correct, and further calculations have been made to obtain the standard free energy of dissociation of S_2 using the other possible spectroscopic values.

A small correction to the pressure calculated by the simple Knudsen formula is necessary to correct for the fact that not all of the molecules vaporizing from the surface of the material whose pressure is being measured hit the top of the cell. The correction for this can be found in papers by Whitman[7] and Clausing.[8] Table II gives the values needed for this correction. The nomenclature is that of Whitman.[7] $W_B = 1$, since the orifice edge was sharp. No attempt was made to supply the correction for the accommodation coefficient not being equal to one. Since agreement within 50 pct is obtained between the experimental results from this work and that calculated from other data, see Fig. 2, it is presumed that for S_2, $\alpha > 0.5$. For this value of α, the correction[9] for $\alpha = 1$ is to add 2 pct. This is neglected, since the exact value for α is not known. For sulfur, the value of α should be very close to one.

Using the Knudsen formula, as modified by Whitman,[7] and the assumption that S_2 and sulfur effuse independently and without interaction, the following formula is easily derived

$$\frac{(WL)}{(A)(K)} = K_1^{1/2} P_{S_2}^{1/2} M_a^{1/2} + P_{S_2} M_{S_2}^{1/2} . \qquad [1]$$

The symbols are identified as follows: K_1 is the dissociation constant for diatomic sulfur going to monatomic sulfur, K has the same definition as that given by Whitman,[7] P is the pressure of the species in question in atmospheres, A is 2658 times the orifice area in sq cm times the duration of the run in minutes divided by $T^{1/2}$, M is the molecular weight of the particle under consideration, and WL is the weight loss of the cell during the run.

The results of the above calculations are shown in Fig. 2. Curves L, M, N, and O show $(WL)/(K)(A)$ calculated from Eq. 1, using the various energies of dissociation of S_2 from spectroscopic data,[10] and for curve L from gas density measurements by von Wartenburg and by Nernst.[1]

In Fig. 2 these same values, obtained in the experiments reported here, are tabulated. It is seen that these data fall between the values of $(WL)/(K)(A)$ from the two lowest values for the spectroscopic energy of dissociation. Although the precision of the Knudsen data reported here is not sufficient to say definitely which of the spectroscopic values is correct, the data presented here support the selection by Chipman and St. Pierre[11] of $\Delta E°_0 = 83.0$ kcal. Additional experimental work needs to be done, using a sulfide with a sulfur potential amenable to Knudsen orifice measurements at higher temperatures, where the contribution of the monatomic sulfur will be much larger than that of diatomic sulfur. Then a better estimate of $\Delta E°_0$ could be made by comparing these data with thermal or equilibria data, as has been done here.

Conclusion

It has been demonstrated that Knudsen cell measurements on the system FeS-Fe-S gas give good agreement with the pressure of S_2 calculated from H_2-H_2S equilibria determinations, if correction is made for the sulfur atoms present in the gas phase above Fe-FeS.

Acknowledgment

This work was sponsored by the Office of Naval Research. Robert Miller assisted in the experimental work reported here. The chemical analyses were done by Caroline Shaffer of the Metals Research Laboratory, Carnegie Institute of Technology. The zircon crucibles were donated by the Laboratory Equipment Co., and the small *cemented diamond particle* wheels, by the Koebel Diamond Tool Co.

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Precipitation of Metal from Salt Solution By Reduction with Hydrogen

Early work on chemical precipitation of metals from metal salt solutions is reviewed. The chemistry and thermodynamics of precipitating copper, nickel, cobalt, and cadmium metals by reaction with hydrogen are discussed. Mechanisms of metal precipitation, nucleation, growth, and agglomeration are reviewed, as well as some solubility phenomena of gases and solids at elevated temperatures. Experimental data presented deal mainly with the reaction of copper sulfate solution with H_2.

by F. A. Schaufelberger

METAL can be recovered from a leach solution either indirectly by precipitation as a compound that is later reduced or directly by electrolysis, cementation, or chemical reduction, for example, with hydrogen. The widely used electrowinning processes suffer from the inefficiency of converting fuel to low voltage dc and from low current efficiency when complete recovery is attempted. With the batch hydrogen reduction methods outlined here, a unit of fuel converted to hydrogen in modern gas reform plants will make two to three times as much metal as can be obtained with electrolysis. With continuous hydrogen reduction, four to six times as much metal is obtained.

Precipitation by reducing a metal salt solution with H_2 has been known for almost 100 years.[1] Commercial use of the process, however, awaited the research and development program initiated by Chemical Construction Corp. Within the last few years this program has brought about construction of commercial plants, listed on p. 701.

Ideal hydrogen reduction will precipitate a pure metal from a solution obtained by commercial leaching methods at a rapid rate without excessive temperatures and pressures. The metal precipitate will be of desired size and density, less than a percent left in the vessel being deposited on the wetted parts.

The present discussion will outline Chemical Construction Corp.'s early development program and will discuss the chemistry and mechanics of reducing copper, nickel, cobalt, and cadmium from solution by H_2. Work on selective reduction of nickel from cobalt has been described earlier.[2]

The article is not concerned with precipitation of copper by disproportionation of cuprous solutions where yield is limited[3] to 50 pct.* It does not discuss use of gaseous reducing agents other than hydrogen, such as SO_2,[4] which may lead to contamination with sulfur, or CO,[5] which is considerably more expensive than hydrogen and produces a gaseous reaction product, CO_2.† The article does not include use of other nongaseous reducing agents,[7] which are far more expensive than CO. Also, notes on the history, engineering design, and performance of commercial plants have been given elsewhere.[8]

It will be shown that a pure metal can be precipitated by reduction with hydrogen from solutions obtained by commercial leaching methods when the solution composition is controlled and proper acidity, proper metal ion concentration through controlled complex formation and hydrolysis, and adequate agitation for suspension of metal and for transfer of reducing gas are maintained. Reasonable temperatures and pressures are used which are less excessive than those used by previous workers, although they are maintained at above equilibrium values because of process kinetics.[9]

It has also been found necessary to induce nucleation and to control growth and agglomeration in order to get a powder product of suitable physical properties.

* Copper precipitation by disproportion, $2\,Cu^{+} = Cu^{o} + Cu^{++}$, is due to instability of the cuprous ion. Cuprous ion can be stabilized by formation of complexes, e.g., with CO or ammonia. Removal of CO from a $Cu_2(CO)_2SO_4$ solution by boiling or by application of vacuum, or the neutralization of a cuprous ammine solution with acid, will cause copper precipitation.

† Formation of toxic nickel tetracarbonyl by reaction of CO on ammoniacal nickel solutions (180°C, 300 psi CO) is discussed in ref. 6.

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Review of the Literature

Muller, Schlecht, and Schubardt of I. G. Farben[10] claimed a successive reduction of silver, copper, nickel, cobalt, and zinc from ammoniacal solution by applying progressively higher temperatures and hydrogen pressures. Metals produced by this technique were not pure, since no attempt was made to adjust the solution composition between the different reductions. It is doubtful that the zinc product contained any metallic zinc.

The major contribution to the literature[11] was made by the Ipatiews,[12] who prepared platinum, iridium, copper, nickel, cobalt, lead, tin, arsenic, antimony, and bismuth at often extreme conditions, up to the critical temperature of water (373°C), at 1500 to 7500 psi, for as long as several days. Even cadmium and zinc were claimed to have been observed in trace quantities precipitated together with basic salts. In the early experiments solutions were not stirred. Extensive formation of oxides and basic salts occurred, probably long before sufficient hydrogen could be supplied in the unstirred liquid to decrease the metal concentration in solution by reduction. The importance of hydrogen pressure was

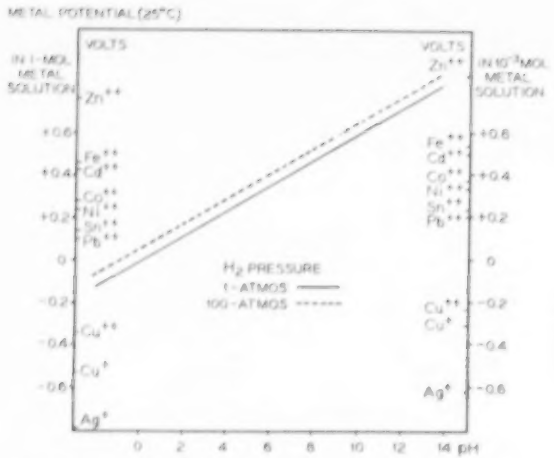

Fig. 1—Potential of 1 and 10^{-3} molar metal solutions, and hydrogen potential at varying pH (25°C).

overemphasized. The pioneer work of the Ipatiews has been continued in Russia[13] with the most recent report by Tronev, Bondin, and Khrenova[14] on reduction of copper, nickel, cobaltous and cobaltic ammoniacal chloride and sulfate solutions with hydrogen. Most of this work, however, was carried out in unbuffered solutions.

Reduction Equilibrium

A. Calculation of Equilibrium: Reduction of divalent metal ions such as copper, nickel, cobalt, lead, and cadmium by hydrogen may be written as

$$M^{++} + H_2 \rightleftarrows M^{\circ} + 2H^{+} \qquad [1]$$

with an equilibrium constant K (neglecting activity coefficients)

$$K = \frac{[H^+]^2}{[M^{++}]P_{H_2}} \qquad [2]$$

where brackets denote molar concentrations and P the pressure in atmospheres.

The degree to which this reaction occurs is given by the familiar thermodynamic equation for the free energy change ΔF (cal) or, more conveniently, the potential E (volt):

$$\Delta F = -23{,}060\ n\ E = -RT \ln K. \qquad [3]$$

Reductions of copper, nickel, and cobalt solutions with H_2 attain commercially attractive rates only at temperatures higher than 70°C. Extrapolation of thermodynamic data is certain to be speculative, but actual data at elevated temperatures are not available. It is therefore convenient first to calculate E for room temperature conditions, then to attempt to approximate E for elevated temperatures, and finally to discuss briefly the effect of variation in experimental conditions.

Fig. 1 plots the variation in E at 25°C for 1 and 0.001 M concentrations of the metal ions of interest, and also the hydrogen potential at various pH values and at 1 and 100 atm H_2 partial pressure (fugacity at 100 atm and 25°C = 106.1 atm[15]). Of course, the metal potential is affected by pH only indirectly, since the metal concentration is a function of pH due to complex or hydroxide formation. For reduction to proceed, the hydrogen potential must exceed the metal potential. It appears possible to reduce metals up to cadmium, perhaps including iron but

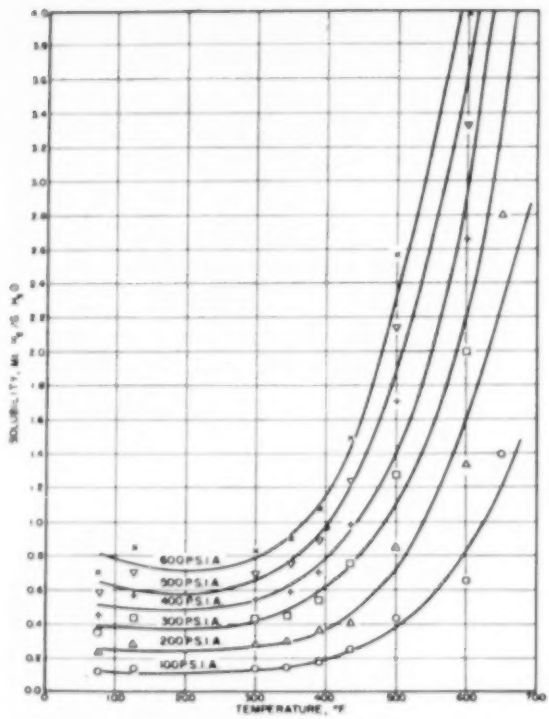

Fig. 2—Solubility of hydrogen (standard temperature and pressure) in water at varying temperatures and pressures. (From *Industrial and Engineering Chemistry*, 1952, vol. 44, p. 1147.)

hardly zinc. Cadmium turned out to be the least noble metal to be precipitated in pure form at industrially satisfactory yields and rates.

It will be noted from Fig. 1 that a hundredfold increase in hydrogen pressure is comparable to an increase of one pH unit.

Calculating reduction equilibria in aqueous solution for elevated temperatures is difficult in view of the uncertainty in estimating the effect of temperature on the entropies of solutes, ions, or undissociated molecules. Since there are ions on both sides of the equation, temperature changes in entropies were assumed roughly to cancel out. This is admittedly not a very good approximation, but it appears as good as any in the absence of experimental data. Eq. 4 was used to calculate reduction equilibria using room temperature data:

$$\Delta F_T = \Delta F_{298°K} - \Delta S_{298°K}\ (T - 298). \qquad [4]$$

It is based on the assumption that the reaction entropy at temperature, T, ΔS_T, is equal to the reaction entropy at 25°C, $\Delta S_{298°K}$. Most of the data were taken from Latimer,[16] but for cobalt and nickel the data obtained by Haring[17] were selected. Data by Cobble[18] and Yatsmirsky-Grafova[19] were used to compute entropies of the ammine complexes.

B. Solubility of Solids and Gases in Water at High Temperatures: Solubility of most metal compounds in water increases with temperature up to 120° to 150°C but then decreases with further increasing temperature and becomes zero at temperatures approaching the critical temperature of water, 373°C.[20] Even at 250°C, solubility of most metal sulfates has decreased to less than 1 gpl. At elevated temperatures solubility of basic metal salts and hydroxides is also markedly decreased, and they

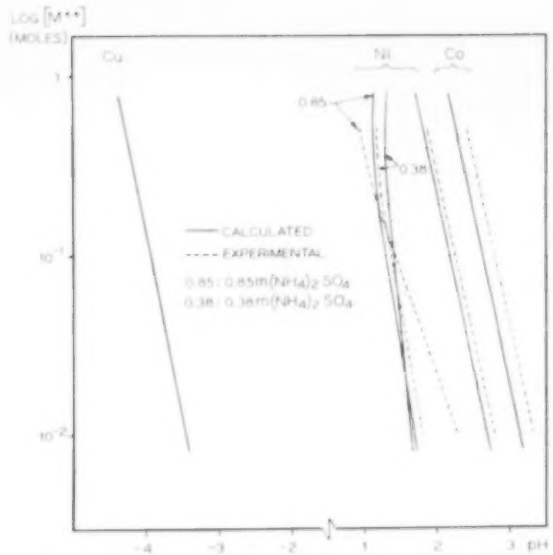

Fig. 3—Reduction equilibria of $CuSO_4$, $NiSO_4$, and $CoSO_4$ in aqueous solution with H_2 (490 psig partial pressure). Reductions carried out at 200°C. pH measurements taken after quenching to 25°C. Calculated figures are computed for 200°C for solutions containing no $(NH_4)_2SO_4$. For Ni solutions containing $(NH_4)_2SO_4$, computation includes cooling to 25°C. (Reprinted from *Transactions of the Institution of Mining and Metallurgy*, London, 1954/1955, vol. 64, p. 379.)

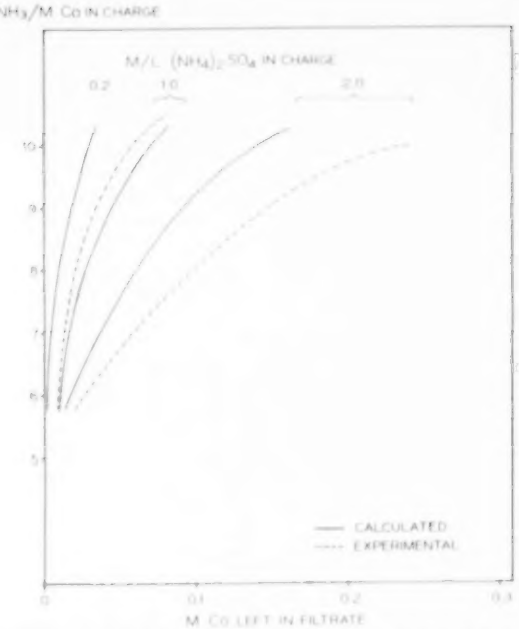

Fig. 4—Reduction equilibrium of cobaltous ammine sulfate with H_2 at 200°C and 500 psig H_2 partial pressure.

will often precipitate out at reduction temperatures from solutions of considerably higher acid strength than at room temperature. The experience of early investigators is so full of references to such precipitates that it is easy to see the importance of controlling solution composition and using temperatures below 250°C to achieve pure metal precipitates. Of course, some high temperature precipitates may reduce as a solid phase and others may redissolve as the reduction proceeds; others may influence the reduction favorably, as hydrogen activators or as nuclei. In reduction from ammoniacal solutions hydrolysis is particularly important, but the present discussion will have to be limited to the reduction of the metal ion only.

Gas solubilities in water, on the other hand, decrease with temperature increase up to about 80°C and then markedly increase with further increasing temperature,[7] see Fig. 2.

The unusual trend in gas solubility has been associated with the change in the structure of water from quasi-crystalline at room temperature to close-packed at higher temperature. At 200°C the structure of water is apparently similar to that of organic solvents, such as benzene, at room temperature[7] and shows similar solvent characteristics. The structure of water is noticeably affected by pressures only above 5000 psi, or above reduction pressures under consideration here.[8]

C. Effect of Reaction Variables: Inspection of Eq. 2 indicates that thermodynamics of metal reduction is favored by a low H^+ concentration, a high M^{++} concentration, and high hydrogen pressure.

1. *Illustrative Experiments:* Table I outlines the results of various experiments qualitatively, illustrating the effect of M^{++} and H^+ ion concentrations on reduction of nickel by hydrogen in various environments. A low nickel concentration was chosen to prevent complication by precipitation of basic nickel salts. The technique is described on page 704.

With nickel chloride, only 5 pct of the nickel was reduced because the H^+ ions that formed during the reduction—HCl being completely dissociated—had reduced the pH to a point where nickel reduction had to stop. In the experiment with nickel sulfate, the moderately stable bisulfate ion is formed and about 10 pct of the nickel was reduced before the solution became too acid. When ammonium sulfate was added to the nickel sulfate, the hydrogen ions produced were increasingly neutralized by formation of bisulfate, and this buffering allowed half the nickel to be reduced before the solution was too acid.

When ammonium acetate was added, the hydrogen ions produced were tied up as largely undissociated acetic acid, and the solution was completely stripped of nickel without becoming too acid. Nickel sulfate plus pyridine reacts to form a weak nickel complex, but pyridine is not a strong enough base, so the solution became too acidic and the reaction stopped.

In the next experiment the nickel was complexed with a stronger base, ammonia, and the solution was buffered with ammonium sulfate. The ammonia raised the pH so that hydrogen became a stronger reducing agent, but it also decreased the concentration of nickel ion in solution by complex formation so that it was harder to reduce. This buffering and complexing also prevented nickel compounds from precipitating in the alkaline solution.

In the experiment with KCN, the concentration of

Table I. Hydrogen Reduction of Various Nickel Solutions*

Solution	Approximate Reduction at Equilibrium, Pct	Final pH, Room Temperature
$NiCl_2$	5	1.9
$NiSO_4$	10	2.2
$NiSO_4$-$(NH_4)_2SO_4$	50	1.6
$NiSO_4$-NH_4 acetate	100	4.1
$NiSO_4$-pyridine	70	2.0
$NiSO_4$-NH_4-$(NH_4)_2SO_4$	98	9.8
$NiSO_4$-KCN	0	11.0

* Ni = 0.2 *M*; temperature = 200°C; H_2 pressure = 1000 psig.

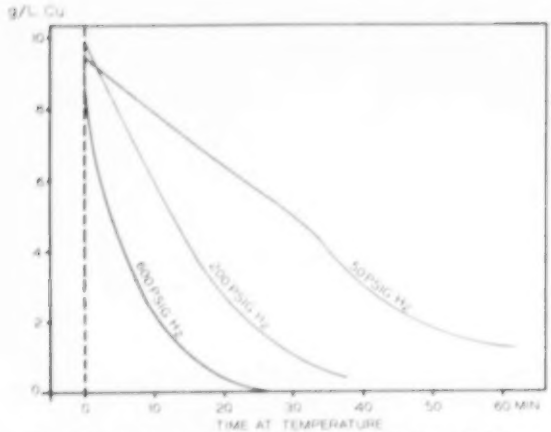

Fig. 5—Rate of reduction of $CuSO_4$ solution with H_2 at 204°C and with varying H_2 partial pressures. Charge, gpl: 10 Cu as sulfate, 5 Fe as sulfate, 120 H_2SO_4, 200 $(NH_4)_2SO_4$, and 80 Cu powder.

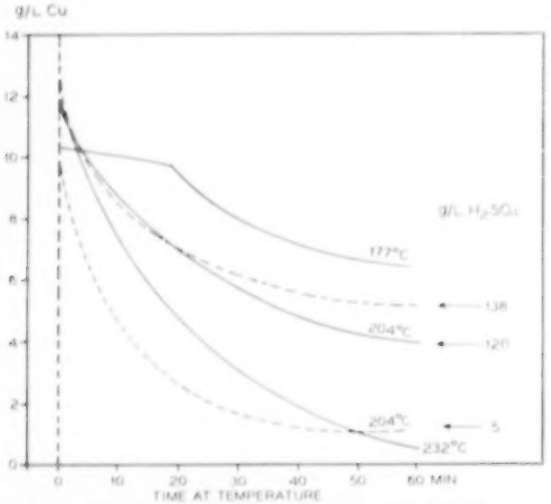

Fig. 6—Rate of reduction of $CuSO_4$ solution with H_2. Charge, gpl: 10 Cu as sulfate, 5 Fe as sulfate, 120 H_2SO_4, or as indicated, 80 Cu as powder; 200 psig. H_2 partial pressure. Varying temperatures (177°, 204°, 232°C at 120 H_2SO_4) and varying initial acid concentrations (5, 120, 138 gpl H_2SO_4 at 204°C).

nickel ion in solution was so low, because of CN^- complexing, that reduction could not be obtained even at pH 11.

2. *Effect of Hydrogen Ion Concentration:* The equilibrium concentrations of copper, nickel, and cobalt sulfate were calculated from Eq. 4 and available room temperature data. Accordingly the free energies of reduction for $CuSO_4$, $NiSO_4$, and $CoSO_4$ are somewhat more negative, i.e., more favorable at 200°C compared with 25°C. The difference appears negligible for copper and amounts to not more than 1 to 2 kcal for nickel and cobalt.

Autoclave experiments were run to determine at 200°C and 490 psi hydrogen partial pressure the nickel and cobalt concentrations in equilibrium with hydrogen at various pH values.[8] Results of experiments and calculations are shown in Fig. 3. Ordinate values represent the molar concentrations of the dissolved metal. The calculated pH values pertain to the reaction temperature; the experimental pH values were of necessity obtained at room temperature after cooling a sample from the autoclave. However, the pH at room temperature is expected to approximate the actual hydrogen ion activity at 200°C because the stable HSO_4^- ion appears to become even more stable with rise in temperature. It will be noted that copper can be essentially quantitatively reduced in strong acid solutions with a calculated pH of −3, or 1000 *M* acid. Although this could not be checked experimentally, complete reduction has been obtained from sulfuric acid solutions as strong as 20 pct. The data also show that cobalt and nickel can be reduced to 0.01 *M* (0.6 gpl) at pH values of 3.3 and 2.75 respectively.

Selective reduction at controlled acid strength is indicated for commercially acceptable separation of copper, nickel, and cobalt from each other and from other metals likely to be found in leach liquors, for example, iron, zinc, aluminum, and magnesium. Experiments in stepwise selective reduction which show the sharp separation of two metals with potentials as close as those of nickel and cobalt have been reported in another paper.[8]

Data on the effect of ammonium sulfate on reduction of $NiSO_4$ are also included in Fig. 3. With ammonium sulfate present, reduction appears to proceed to a lower pH value before equilibrium is reached. The pH is chiefly determined by the bisulfate-sulfate buffer system. The second dissociation constant of H_2SO_4, which is 1.25×10^{-2} at 25°C has been estimated to be 5.1×10^{-4} at 200°C. The hydrogen ion activity at reduction equilibrium therefore will increase upon cooling and furnish a pH somewhat more acid than the actual acidity at reduction conditions, satisfying the expression:

$$k_{200°C} = 1.25 \times 10^{-2} = \frac{[H^+]\,[SO_4^=]}{[HSO_4^-]} \qquad [5]$$

In contrast to the above discussed reductions without ammonium sulfate, these equilibria with ammonium sulfate were calculated for room temperature, using Eq. 5 to convert the equilibrium computed for 200°C to room temperature.

For calculation purposes the activity of the metal ion at 200°C was assumed to be 1 and about 0.1 in the presence of ammonium sulfate, taking into account the formation of sulfate complexes.[28] Experimental data checked the calculated data closely enough to support the assumptions made.

Additional experiments studying the reverse reaction, the dissolution of metal in H_2SO_4 under H_2 pressure, gave an order of magnitude agreement. It is interesting to note that while nickel metal dissolves easily in 1 pct H_2SO_4 to produce H_2 gas at atmospheric pressure, 500 psi H_2 partial pressure will stop nickel dissolution in 1 pct H_2SO_4—0.5 *M* nickel solution.

3. *Effect of Metal Ion Concentration:* Metal ion concentration depends upon complexing and also pH which controls the precipitation of basic compounds.

Ammonia is an economical reagent for raising the pH of the solution and thus obtaining a more favorable thermodynamics for metal reduction. On the other hand, ammonia is also an efficient complexing agent for copper, nickel, cobalt, and cadmium, and the metal ion concentration in such solutions is therefore considerably diminished according to:

$$k_x = \frac{[M^{++}]\,[NH_3]^x}{[M(NH_3)_x^{++}]} \qquad [6]$$

In Table II overall dissociation constants k_x and standard potentials are given for a number of metal

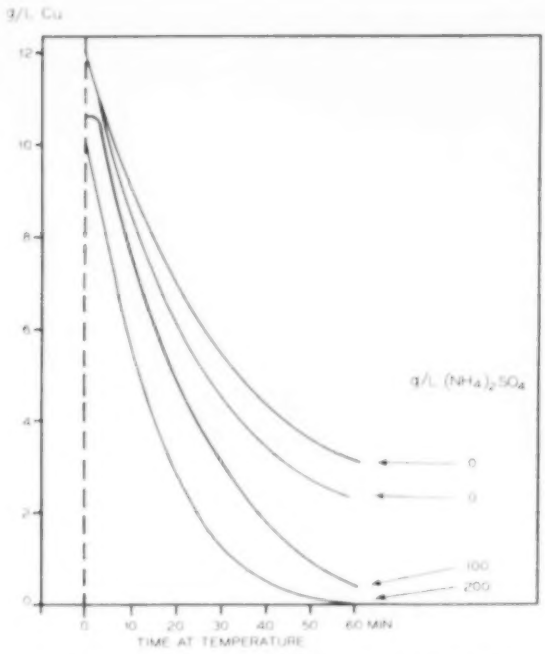

Fig. 7—Rate of reduction of $CuSO_4$ solution with H_2 (200 psig partial pressure) at 204°C, with varying sulfate concentration. Charge, gpl: 10 Cu as sulfate, 120 H_2SO_4, 80 Cu powder; 5 Fe as sulfate, except second curve from top: 15. $(NH_4)SO_4$ as indicated.

ammines. "$\frac{N}{Z}$ log k + log 55" data are also included. This expression was introduced by Bjerrum a few years ago[20] as a more convenient way for expressing the strength with which the ligands are held. N is the number of uniformly bound ligands, Z the corresponding coordination number, and k the mean complexity constant of the system.

It should be noted that due to the decrease of metal ion concentration the potential for the ammine is higher. However, the increase is less than the increase in the hydrogen potential with a change from acid to ammoniacal solution, and all these complexed solutions are thermodynamically reducible by hydrogen from ammoniacal solution.

In contrast to its behavior in acidic solution, bivalent cobalt in ammoniacal solution is more noble than nickel. This is due to the increased dissociation of the cobaltous ammine complex, the dissociation constant being 1.25×10^{-5}, as against 1.8×10^{-9} for nickelous ammine.

Also it appears that a certain nickel-cobalt separation can be obtained in acid but that in ammoniacal solution cobalt should reduce ahead of nickel. However, some selective nickel reduction has also been obtained in ammoniacal solution.[16, 17] This indicates that nickel reduces at a faster rate than cobalt.

The reduction of divalent metals from ammoniacal solutions may be written:

$$M^{++} + 2NH_3 + H_2 = M^{\circ} + 2NH_4^{+} \qquad [7]$$

or

$$K = \frac{[NH_4^{+}]^2}{[M^{++}]\,[NH_3]^4\,P_{H_2}} = \frac{[NH_4^{+}]^2 \cdot [NH_3]^{z-4}}{k_z \cdot [M(NH_3)_z^{++}]\,P_{H_2}} \qquad [8]$$

Evaluating this equation at 200°C with room temperature data again requires the simplifying assumptions used with Eq. 2. This gives $K_{Ni^{++}} = 4.78 \times 10^{6}$ for the reduction of $Co(NH_3)_6^{++}$. Assuming $k_{Ni^{++}} = 4 \times 10^{-9}$, activity coefficient of $NH_3 = 0.5$, and of NH_4^{+} and the ammine complex = 0.2, the curves of Fig. 4 were obtained. These curves were checked by experimental reduction for 0.2 and 2.0 mols per liter $(NH_4)_2SO_4$.

The presence of k_z in the denominator in Eq. 8 indicates that reduction of weak complexes is favored. It is apparent that high concentrations of ammonium salts and free NH_3 (except in diammine reduction) adversely affect the reduction equilibrium, see Fig. 4.

Eq. 8 is valid only for one particular complex, whereas actually a number of different complexes exist that should be taken into account in an exact treatment of the system. It should be remembered that during the course of the reduction the total metal ion concentration decreases and $2M$ NH_3:M metal are converted to $(NH_4)_2SO_4$. For example, if a mol ratio of 4 NH_3:Co is used at the start, after 90 pct reduction the mol ration is 22 NH_3:Co. With increasing NH_3:Co ratio the complexing increases and cobalt ion concentration decreases much faster than the total cobalt concentration. It would seem that the use of more than 2 NH_3:Co would be undesirable because the reduction would not go to completion. However, the lower ammines are not very stable at reduction temperatures, and an ammonia ratio initially somewhat above 2 may be required to prevent hydrolysis. Hydrolysis can also be minimized by adding $(NH_4)_2SO_4$. In commercial

Table II. Copper, Nickel, and Cobalt Ammines*

Standard Potential (25°C) (volts)			Dissociation Constant of Ammine	
Ionic Solution	Ammine Solution		k_z	$\frac{N}{Z}$ log k + log 55
	$Cu(NH_3)_2^{+}$	+ 0.12	1.35×10^{-11}	7.2
Cu^{++} + 0.337	$Cu(NH_3)_4^{++}$	+ 0.05	4.7×10^{-13}	5.0
Ni^{++} + 0.231	$Ni(NH_3)_6^{++}$	+ 0.49	1.8×10^{-9}	3.2
Co^{++} + 0.278	$Co(NH_3)_6^{++}$	+ 0.42	1.25×10^{-5}	2.6
	$Co(NH_3)_6^{+++}$		2.2×10^{-36}	7.6

* According to Latimer, ref. 16.

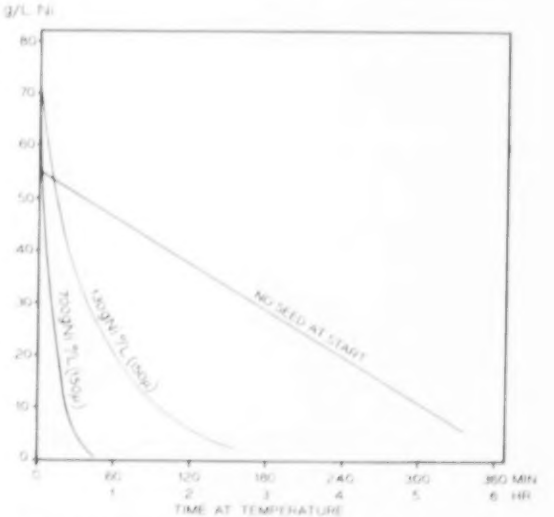

Fig. 8—Rate of reduction of nickel. Tetrammine sulfate solution at 232°C with 450 psig H_2 partial pressure, with and without nickel seed.

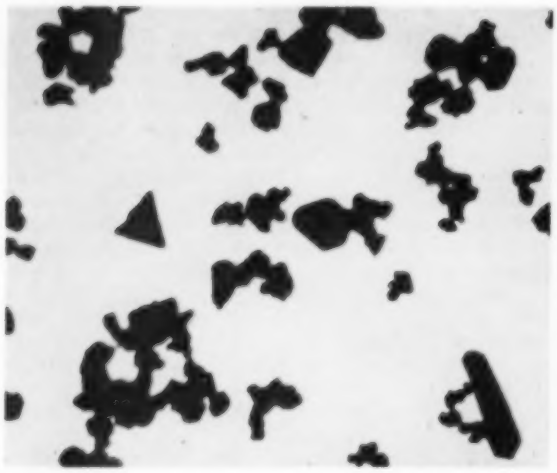

Fig. 9—Crystalline copper precipitated at 80°C from $Cu_x(CO)_ySO_4$ solution by slow disproportionation. X300.

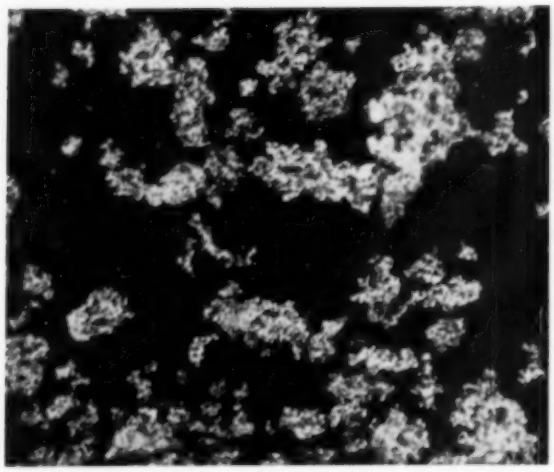

Fig. 10—Copper powder. H_2 reduced from $CuSO_4$-H_2SO_4 solution at 200°C. No seed. Agglomerates of crystals are result of precipitation by H_2 at high reaction rate in commercial-type reaction. X25.

practice, in cobalt reduction 3 NH_3:Co is used with 0.4 *M* $(NH_4)_2SO_4$ while in nickel reduction about 2 NH_3:Ni is used with up to 2 *M* $(NH_4)_2SO_4$. In other words, extra ammonia has been found better for cobalt and extra $(NH_4)_2SO_4$ has been found better for nickel in order to control both precipitation of nonmetallic compounds at the beginning of the reduction and the adverse effect of high NH_3:metal and high $(NH_4)_2SO_4$ at the end. The situation is even more involved when ammoniacal copper carbonate solutions (scrap copper leach liquor) are reduced. Copper in ammoniacal solution is present in two valence states and numerous complexes between Cu', Cu'', NH_3, and carbonate exist. When CO is used as reducing agent, additional complexing of Cu' with CO occurs. Not only is the picture complex at the start; the situation becomes more complicated during the course of reduction as NH_3 and CO_2 are liberated, resulting in an increase of their partial pressures and a corresponding decrease of the partial pressure of the reducing gas.

4. Effect of Hydrogen Pressure: Data in Fig. 1 show that increasing hydrogen partial pressure has small effect on reduction equilibrium compared to the effect of pH. Use of high H_2 partial pressures is therefore not justified thermodynamically.

Mechanics and Kinetics

It has been pointed out that high pressures and temperatures are not needed for hydrogen reduction of most metal solutions. Yet commercial operation in plants using hydrogen reduction employs temperatures of 140° to 200°C and pressures of 400 to 800 psig, of which at least half is H_2 partial pressure. These conditions, according to present knowledge, have been found justifiable in order to obtain commercial reduction rates. They are still far less than those used by earlier investigators.

For a useful process it is not enough merely to make metal from its solution at a reasonable rate. It is also necessary to get the metal product in a form suitable for discharge from the reduction autoclave, that is, as a sand-sized powder product rather than as plate on the walls of the autoclave or as pebbles. Obtaining metal in suitable form is also a kinetic rather than an equilibrium phenomenon.

It is readily admitted that at the present time no attempt to formulate a complete kinetic explanation of metal reduction can reasonably be contemplated. Furthermore, the diversity of reduction kinetics makes the experimental picture very complex to present in full. To maintain the introductory character of this article an illustrative discussion is presented of the mechanics and kinetics of the reduction process and semiquantitative data on one system only, the reduction of $CuSO_4$ with H_2.

A. Effect of Reduction Conditions: Primary controllable variables in hydrogen reduction are hydrogen pressure, temperature, solution composition, amount and kind of seed metal added, and agitation employed.

Example: Reduction of $CuSO_4$: The investigation was carried out with dilute copper solution to approximate the conditions of the last compartments in a continuous reduction system where the rates will be least. Also, complications due to possible formation of nonmetallic precipitates are avoided. Preliminary experiments on reproducibility indicated that data can be reproduced to a fair degree if heat-up effects are ignored. Some seed (oxidized surface) is leached during the heat-up period and causes some difference in copper concentration at zero time. The ordinates in Figs. 5 to 8 indicate concentration of metal remaining to be reduced.

1. Hydrogen Pressure: Effect of variation of the hydrogen partial pressure is shown in Fig. 5. The straight line portion of the curves in Fig. 5 at the lower hydrogen partial pressure indicates that the reaction may be controlled by dissolving hydrogen, but at the higher partial pressure this effect disappears.

2. Effect of Temperature: A similar set of experiments was run with fixed hydrogen pressure at various temperatures. Results are shown in Fig. 6. It may be noted that the rate is considerably increased with temperature.

3. Effect of Acidity: Also included in Fig. 6 are curves for reduction of solution with varying concentrations of acid initially present. The adverse effect of acid on the reduction equilibrium was noted in the theoretical discussion. Rate of reduction is also reduced by increasing acid strength.

4. *Effect of Sulfate:* Presence of sulfate, on the other hand, $(NH_4)_2SO_4$ or $FeSO_4$, for example, increased the rate considerably, as shown in Fig. 7.

5. *Effect of Seed:* In all the experiments of this section 80 gpl of copper seed was present. Seed used in these experiments was produced by disproportionation of an ammoniacal cuprous sulfate solution by acidification. Under these conditions the copper powder product consists mostly of octahedral crystals as illustrated in Fig. 9. Increase in copper powder hardly increases the rate of reduction. This is in marked contrast to conditions in nickel or cobalt reduction, Fig. 8.

6. *Effect of Agitation:* It has been mentioned that certain reduction tests gave a slow rate because they were diffusion-controlled. It will be shown below that the use of seed is frequently desirable to activate H_2 or to facilitate growth. To avoid diffusion-controlled reactions and to suspend the seed metal powder, adequate agitation is needed. In general this is intense agitation designed to keep the solids suspended and to maintain a good gas-liquid transfer. This is important for reactions carried out in expensive pressure vessels where economic considerations require that reaction time be maintained at a minimum. Although above tests on $CuSO_4$ were all carried out with the same agitation, experimental reduction data should always be taken as relative, and unfortunately comparison and scale-up of agitation, particularly for such complex reaction systems, are still far from being fully understood.

B. General Mechanism: Figs. 9 to 16 indicate the nature and variety of the powder product obtained from reductions. It may be noted that the usual metal product is highly agglomerated, but well formed crystalline metal particles can be obtained.

Metal preparation by reduction of the metal ion from solution with H_2 is composed of nucleation, growth, and agglomeration phenomena. Nucleation is the homogeneous formation from the metal ions of the smallest stable particle of metal. Growth for the present purposes is the atom-by-atom deposition of metal onto a solid surface, whether a metal or foreign surface. Agglomeration is the clustering of two or more metal particles to form an aggregate which can be permanently cemented together by an overgrowth of metal.

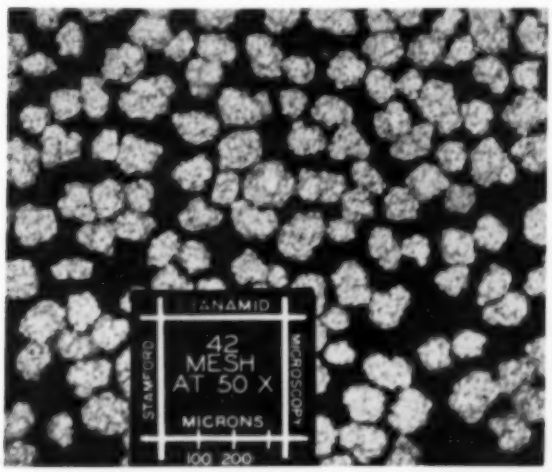

Fig. 11—Nickel powder, H_2 reduced from $Ni(NH_4)_2SO_4$-$(NH_4)_2SO_4$ solution at 200°C, on seed. X50. For cross section see Fig. 12.

- The Chemico metals technique is proving its worth, as several plants are now operating close to or at capacity and consistently produce copper, nickel, and cobalt of commercially attractive purity at competitive costs.
- Having met contract performance, American Cyanamid Co. turned over operation of the Calera plant of Howe Sound Mining Co. to its owners on Dec. 8, 1955. A practical commercial operation, the plant is reported to have produced in March 250,000 lb of cobalt containing 3 to 4 pct Ni.
- Sherritt Gordon operations for 1955, including an ammonia leach of the company's own design, have already been reported as satisfactory and are said to have exceeded plant capacity. Twenty-five tons of nickel per day and some cobalt are now produced.
- National Lead's Fredericktown plant for recovery of copper, nickel, and cobalt from 50 tpd of low grade sulfide concentrate is said to operate at about two-thirds capacity.
- The Whitaker Metals Co. scrap copper leach plant has recovered as much as 240,000 lb per month of a premium product for the copper metal powder market. The plant is now operated by Fluor Corp. as a semi-pilot plant.
- Freeport Sulphur Co.'s demonstration plant for recovery of nickel and cobalt from 50 tons of Cuban laterite per day is reported to be operating satisfactorily at full capacity.
- Chemical Construction Corp., which did all the early research and development work and the design and construction of the plant, was sold by American Cyanamid Co. to Ebasco in April 1956. Negotiations are in progress for sale of the metals processes patents.

Earlier kinetic and electron microscopy study on gold sols by Turkevich et al. should be mentioned.[28]

Qualitative reducibility of a given metal ion naturally depends on the chemical nature of the metal ion, that is, on whether the ion is complexed by water, chloride, ammonia, or even organic molecules. Cadmium acetate, for instance, appears to reduce much more rapidly from an alcohol solution than from an ammine complex in an aqueous solvent.

Metallic cadmium was precipitated in small yields by H_2 reduction from several ammine sulfate solutions at 224°C and 1200 psi total pressure. A particularly pure metal product, however, is obtained in good yield, 65 and 80 pct, respectively, from a 0.5 *M* cadmium acetate solution in methanol or isopropanol at 200°C and 500 psi H_2 partial pressure.

In this connection it may be noted that cobalt ammine complexes often are markedly stable from a kinetic viewpoint.[29]

1. *Nucleation:* Homogeneous nucleation of metal particles is usually difficult compared to their growth. For example, reduction of copper, nickel, and cobalt from ammoniacal solution will usually nucleate only with difficulty but will readily grow additional metal onto metal surfaces already present. On the other hand, reduction of copper from acidic solution nucleates (and grows) readily, presumably merely because a larger number of metal ions are available in acidic solution. In ammoniacal solution the problem is therefore one of supplying a metal surface, or seed, for growth. In early work at Chemical Construction Corp. this was accomplished by grinding the oversize metal product. However, grinding is cumbersome and a source of contamination of the product; also it is not possible to restore the original internal surface of the early precipitates. It soon became evident that improved means of nucleation had to be developed, such as: 1) use of a nongaseous

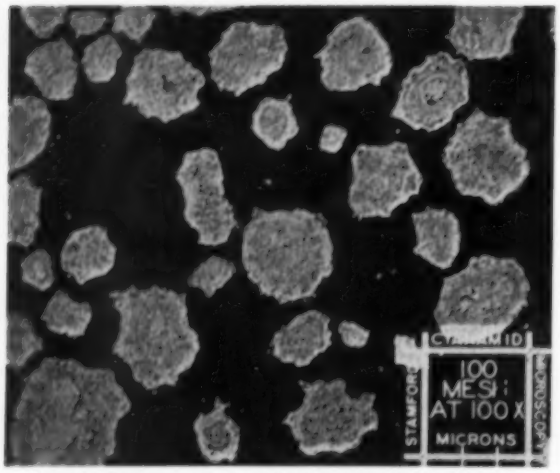

Fig. 12—Cross section of a Fig. 11 type of nickel powder. H_2 precipitation from ammoniacal sulfate solution on seed. Note growth by agglomeration and deposition (onion structure). X100.

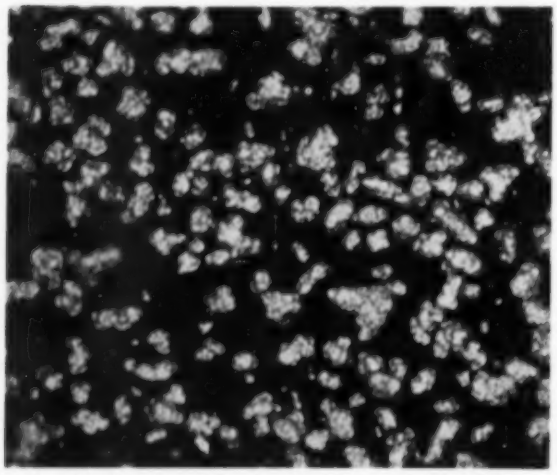

Fig. 13—Nickel powder. H_2 reduced from acidic $NiSO_4$-$(NH_4)_2SO_4$ solution in continuous operation at 200°C. No seed. X75.

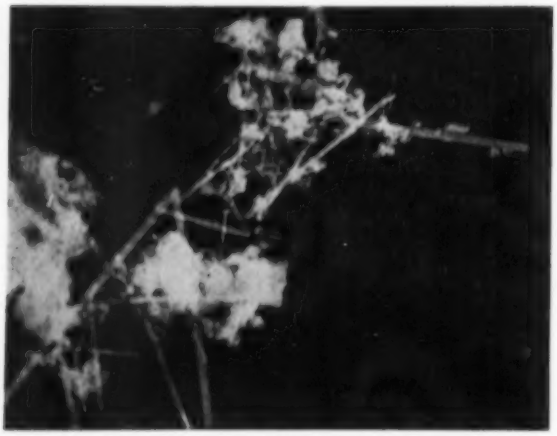

Fig. 14—Electron micrograph of nickel needles from a powder obtained by H_2 reduction of $NiSO_4$-H_2SO_4 solution at 200°C. Area shown is approximately 3μ wide.

reducing agent (e.g., hypophosphite or hydrazine) to produce a fine metal colloid from a minor portion of the solution; 2) performing a self-nucleating acid reduction on a minor part of the solution; or 3) use of solid compounds that catalyze the growth of metal by H_2 reduction.

Nickel and cobalt metal, certain oxides, and various other hydrogen activating compounds are used industrially for hydrogenation of unsaturated organic compounds. It appears plausible that such compounds would also catalyze a metal reduction. Heterogeneous catalysis was indeed found to be important for the nucleation of metal in reduction by H_2, and it happens in the case of nickel and cobalt precipitation that the reduction products themselves are among a number of possible hydrogenation catalysts. On the homogeneous catalytic activation of H_2 by Ag^+, Hg^{++}, or Cu^{++}, see Halpern.[35]

It should be noted that it is often difficult to decide whether in a given reduction run the metal had truly nucleated in the bulk of the solution or whether reduction was initiated on accidental impurities such as dirt or oil from the stuffing box.

2. *Growth:* Crystal growth is a sequence of dissolution, bulk diffusion, surface adsorption, surface diffusion, chemical reaction, deposition, desorption, and other reactions, and the kinetics of growth is concerned with the kinetics of that sequence. Gross reaction rate during a reduction should somehow depend, in a first approximation, upon the effective metal ion concentration, the H_2 molecule concentration (in solution), the metal surface area, and temperature. Other effects of lesser immediate interest include the variation in growth rate between different crystal faces, activity coefficients, and poisoning of the metal surface by adsorption.

Quantitative studies of growth kinetics are severely obscured by agglomeration of particles during reduction, which makes it difficult to determine surface areas. Also, as described above in reduction from ammoniacal solution the varying NH_3:M^{++} and NH_4^+ mol ratios during reduction cause a varying effective concentration of metal ion. For the present purpose, however, it is evident that the amount of surface area is important, see Fig. 8, and that the nucleation reaction noted above should give a high area of metal. The structure of the nickel powder shown in Fig. 12 indicates growth by deposition (onion structure) and agglomeration.

Even the mechanism by which crystal growth occurs is not clear. Recent investigations increasingly support a screw dislocation mechanism for crystal growth rather than the classical two-dimensional, surface nucleation viewpoint. In metal reduction, a filamental type of crystal growth has often been observed which appears to be the result of a dislocation mechanism, see Fig. 14 and ref. 30.

Since cobalt and nickel metal are ferromagnetic, it would perhaps be expected that growth of these metals in a magnetic field would affect the growth kinetics or at least the magnetic properties of the resulting metal crystals. In the laboratory of Chemical Construction Corp. W. G. Courtney has observed an increase in the coercive force of these metals when they were prepared in a magnetic field by reduction with hypophosphite. However, he could observe no effect on the coercive force in reduction by H_2. This suggests a qualitatively different growth mechanism with the two different reducing agents.[31]

3. *Agglomeration:* From colloid chemistry it is known that, unless stabilized, solid particles in the

size range of 0.1 to 5 μ agglomerate. A particle may agglomerate either to another particle or to the autoclave wall. According to theory, the tendency for either type of agglomeration to occur depends upon particle concentrations, surface area of the wall, type and degree of adsorption of ions onto the surfaces of the particles and walls, degree of agitation, and many other factors. Appropriate data at elevated temperature are again lacking; even at room temperature the agglomeration process is not well understood.

Agglomeration is doubly undesirable. Agglomeration between particles decreases the total metal surface area and thus the reduction rate. Agglomeration to the wall, or wall plating, Fig. 15, not only removes metal from the immediate production but also requires equipment downtime for its periodic removal. After plating starts there is a catalytically active metal surface on which additional metal will be easily deposited, unless a much larger surface of metal in the bulk solution is provided in the form of metal seed particles. On the other hand, agglomeration, in cases of slow growth, is the only mechanism available to consolidate small particles to form metal powder coarse enough to prevent its redissolution in subsequent washing steps or dusting in drying operations.

Two observations from separate and dissimilar studies will be given to illustrate the agglomeration process. Successive samples of a $NiSO_4$ reduction conducted at slow rate showed that in the first sample the nonagglomerated particles have a size range of 0.1 to 0.4 μ (by electron microscope). In the second sample taken a few minutes later, the particles are either 0.5 to 0.8 μ or are agglomerates of 2 to 5 μ total diameter.

An autoclave with glass walls (a sight glass) was used to reduce copper from an ammine carbonate solution with CO. As the temperature was increased toward 120°C, a Tyndall effect was noted. A few minutes later, presumably after a critical particle size had been reached, a sudden coagulation occurred which formed a few visible agglomerates in the bulk of the solution and rapidly coated the glass wall with copper foil.

Fig. 15—Nickel foil and agglomerates as stripped from the walls of the autoclave. Reduction of an ammoniacal nickel solution at 175°C with H_2. No seed was provided. Compare with Fig. 13, nickel from an equally unseeded reduction, but from a self-nucleating acid system. X3.

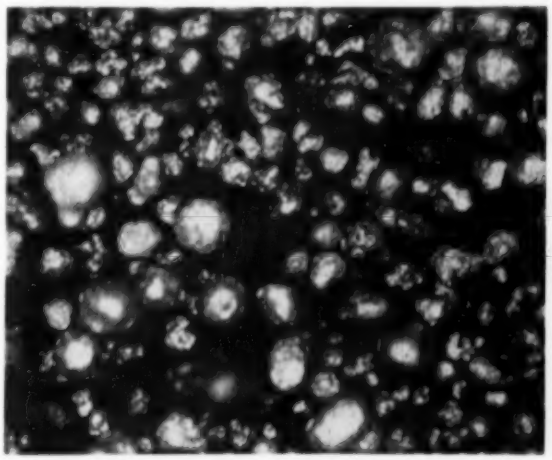

Fig. 16—Cobalt powder. H_2 reduced from $Co(NH_3)_4SO_4$-$(NH_4)_2SO_4$ solution at 200°C, on seed. Highly densified. Note how in contrast to Fig. 11 surface of agglomerate is smoothed out by subsequent metal deposition. X75.

Purity

Impurities in a metal reduction can arise from: 1) superficial entrapments of solid salts or solution during agglomeration of metal particles, 2) entrapment by agglomeration but followed by an overgrowth of additional metal, or 3) an intimate mixture of impurity and metal atoms arising from incorporation of impurity atoms during the atom-by-atom growth of metal during reduction.

Reduction from insufficiently buffered ammoniacal solution at excessive temperatures may lead to impure powders. The fluffy basic metal compounds that precipitate on heating up are likely to retain impurities, and since such compounds normally reduce directly by solid-gas reaction without being redissolved as reduction proceeds, contamination by carbon from carbonate or sulfur from sulfate solution, oxygen, or contained impurities is in certain cases expected.

It is also possible at temperatures near 250°C to reduce sulfate to sulfide with hydrogen. Another reason for using control of environment to facilitate reduction is that such high temperatures are not needed.

Pure metals can also be obtained from impure solutions. Impurities such as iron, zinc, aluminum, and magnesium are not reduced to metal and will not contaminate the metal powder if kept in solution. Copper powder containing 0.005 pct Fe has been produced in acid reduction from solution containing up to 15 gpl Fe^{++}. Even cobalt and nickel, if present, do not contaminate copper if the copper

Table III. Analyses of Copper, Nickel, and Cobalt Powders

	No. 1 Cu	No. 2 Ni	No. 3 Ni	No. 4 Ni	No. 5 Co	No. 6 Co	No. 7 Co
Cu	99.948	0.01	nil	0.037	nil	0.01	0.02
Ni	nil	99.85*	99.72	99.74	0.15	0.54	3.7*
Co	nil	0.1	0.24	0.15	99.6	98.49	95.7
Fe	0.007	0.01	0.025	0.027	0.20	0.08	0.07
Zn	nil		nil				nil
Sn	0.003						
Pb	nil						
S	nil	0.01	0.001	0.015	0.02	0.06	0.05
C	0.011						
H_2 loss	0.008						

* No nickel-copper separation carried out at this plant.
Nos. 1-3 and 5 are products prepared in different piloting operations.[4,20]
Nos. 4, 6, and 7 are plant products.

is reduced from solution with a pH of less than 1 where, as shown by Fig. 3, cobalt or nickel are not reduced at equilibrium conditions. In one commercial operation copper is reduced from a solution richer in nickel and cobalt than in copper and the powder produced analyzes less than 0.01 pct of each, nickel and cobalt.

Copper analyzing 99.99 pct has been produced from sulfate and from carbonate solutions. In Table III a few product analyses from various industrial and larger piloting operations are given.

In general each problem is different and any required purity can be obtained by a combination of controlled reduction with prepurification and subsequent washing.

Apparatus

Experimental data presented here have been obtained during the course of a program of applied research extending over a period of several years. Autoclaves used include rocker bombs, 1-gal autoclaves heated with Dowtherm jackets or with gas and usually equipped with a liner. Temperatures are usually controlled within 2° to 5°C. A few experiments have been run in 10 and 25-gal autoclaves. These are heated with a steam coil.

Although the air in the clave could be removed by heating and venting, because many solutions may contain ammonia, it has been the standard practice to purge the clave with nitrogen before heating.

The pressure vessels were usually provided with sample lines, some having porous stainless steel or tantalum microfilters, for sampling at operating temperature and pressure into sample bombs. In experiments of qualitative nature, the pressure vessels were cooled before discharging, although some redissolution of metal may have resulted.

Considerable quantities of reducing gases are consumed in these reduction reactions. In view of their low solubility, maintenance of good absorption and diffusion rates by suitable stirring is important.[22] Various types of agitation have been employed.

Most of the various physical and chemical reactions that occur during a reduction appear to be greatly affected by what may be called the hydrodynamics or the stirring pattern, which in turn are largely functions of the geometry of the stirrer and vessel, of the stirring rate, of the composition of the solution, and of the reaction conditions. Efficient dispersion of solids (seed metal, catalysts and newly precipitated metal) is as important as good gas distribution. Excessive centrifugal action should be avoided in order not to plaster the autoclave walls with growing metal particles. Rough surfaces are undesirable, as they become coated much faster.

Precipitated powdered metal was usually washed with water, alcohol, and acetone or ether and then dried on a steam bath. In some tests the powders were dried with hydrogen at elevated temperatures.

Acknowledgment

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aime news

Section Award to Honor Frank J. Tone

The Niagara Frontier Section, AIME, has announced the establishment of the Frank J. Tone Award, to be presented annually for outstanding contributions to the fields of mining or metallurgy in this area. The award, honoring the late Frank J. Tone, formerly president of the Carborundum Co., has been endowed by his sons, F. Jerome Tone and Franchot Tone. Announcement of the new award was made by David Swan, Section Chairman, at the banquet Tuesday evening, March 20, in connection with the AIME Regional Reactive Metals Conference, held at Hotel Statler, Buffalo.

A pioneer in the fields of electrothermal abrasives and refractories, Frank J. Tone made many improvements in metallurgical furnaces and methods for their manufacture. He was born in 1868 in Bergen, New York, attending public schools there. After graduation from Cornell University in 1891 as an electrical engineer, he began his business career at the Thomson-Houston Co., followed by two years' service with the Pittsburgh Railways Co. In 1895 he joined the Carborundum Co. becoming plant superintendent, then works manager. He became president of the company in 1919, in which post he served for the remainder of his career. He died July 26, 1944.

Dr. Tone also served as president of the Globar Corp., director in the Power City Bank, president of the Republic Carbon Co., and director of Canadian Carborundum Co. His affiliations included membership in AIME, American Institute of Chemical Engineers, Society of Chemical Industry of London, American Chemical Society; he was also past-president of the Electrochemical Society. Awarded medals at the Paris Exposition in 1900, Pan-American Buffalo 1901, St. Louis 1904, the Schoellkopf Medal of the American Chemical Society in 1931, the Edward Goodrich Acheson Medal and Award of the Electrochemical Society, 1935, and the Perkin Medal Award of the American Chemical Society, 1938, he also received an honorary Doctor's degree from the University of Pittsburgh in 1935.

In 1900 he married Gertrude Franchot, daughter of the prominent N. Y. State Senator. They had two sons, F. Jerome, presently vice president of the Carborundum Co., and Franchot Tone, the well-known star of stage, screen, and television.

Details of the administration of this award will be announced later.

ECPD Submits New Engineering Definition

A new definition of engineering was submitted by the Engineers Council for Professional Development, and approved by the AIME Board of Directors at their February meeting. It states: "Engineering is the profession in which a knowledge of the mathematical and physical sciences gained through study, practice, and experience is applied with judgment to the known materials and forces of nature for the comfort, health, safety, and welfare of mankind."

Laboratory Course At Cornell University

A summer laboratory course in techniques and applications of the electron microscope will be offered again this year by the dept. of engineering physics at Cornell University, Ithaca, N. Y. The two-week course under the direction of Benjamin M. Siegel will run from June 11 to June 23. Guest lecturers include Cecil E. Hall, Massachusetts Institute of Technology, Cambridge, Mass., and Robley C. Williams, University of California, Berkeley, Calif.

The course is designed to provide an intensive survey of basic theory and interpretations of results. Registration is limited to a small group to assure ample facilities for each student to pursue laboratory work in his special field at an introductory or advanced level.

Inquiries should be addressed to: Prof. Benjamin M. Siegel, Dept. of Engineering Physics, Rockefeller Hall, Cornell Univ., Ithaca, N. Y.

Deadline Set for 1957 Annual Meeting Papers

Sept. 15, 1956, is the deadline for the Institute of Metals Div. papers for the 1957 New Orleans Annual Meeting, and the deadline for all Iron and Steel Div. and Extractive Metallurgy Div. papers that can be considered for preprinting. Papers received by this deadline but requiring revision may not be processed in time to permit scheduling for this meeting.

For IMD papers, authors are requested to submit their papers in four copies to Institute headquarters. The IMD Programs Committee, for effective programming, considers papers at the same time they are submitted for publication. The fourth copy will be transmitted to the IMD Programs Committee. The other three copies are needed by the Publications Committee, in accordance with the procedure followed in the past.

EMD and ISD papers should be submitted in three copies.

Sept. 15, 1956 is the deadline for Institute of Metals Div. papers (4 copies) for the 1957 New Orleans Annual Meeting and the deadline for all Iron & Steel Div. and Extractive Metallurgy Div. papers (3 copies) that are to be considered for preprinting. Papers received by this deadline but requiring revision may not be processed in time to permit scheduling for this meeting.

Three Metals Branch Divisions Report on Year's Achievements

IMD Shows Balanced Budget For Year

The Annual IMD business meeting held on February 22, revealed that for the first time in its history, the IMD and the Metals Branch have completed a year of great activity with a balanced budget. This achievement is the result of planning and efforts set in motion several years ago. In 1949 the Metals Branch deficit was $60,686, and advertising income for the year was $13,000. The war had ended and the Branch was caught in the trap of an increasing spiral in both the quantity of research papers and publication charges.

In subsequent years, economies in operation, the expansion of advertising revenues to the $45-50,000 level and an increase in dues from $15-20 per year, have cut this deficit in half. Secondly, recognizing that industry would support a cooperative publication service benefiting industrial metallurgical research, the Board of Directors agreed to the IMD proposal that a Metals Branch Publication Fund be established. The solicitations carried out entirely by members and staff, have netted the fund $66,775 from 68 contributors. It was necessary to proceed cautiously on the publication page budget while the fund was being established. Consequently, this year not as many pages were published as desired. Using $23,184 from the fund during 1955 helped to balance the budget easily. It is hoped that the fund's minimum can be kept at $30,000 annually, which will keep the Branch abreast of new research results.

The executive committee has tackled expansion services to members. Considerable progress has been made along four lines. The reorganization and increased activity of the program committee has made possible additional symposia on subjects of great interest, and an improved arrangement for the presentation of research papers by means of research seminar, research summary, and research-in-progress sessions. We have presented six symposia this year—three in Philadelphia and three at the present meeting. These programs have been responsible for increased attendance, which reached the record figure of 850 at the Philadelphia meeting. The program committee has also been active in the expansion of regional meetings, other than in New England and the northwest where they have been established for some time.

A third direction of progress has been with special committees on powder metallurgy, physics of metals, titanium and nuclear metallurgy. Each committee has contributed at least one symposium this year and the nuclear metallurgy group had two. As a result of the excellent reception afforded the symposium on high temperature metallurgy in Philadelphia, a temporary committee has been formed to study the possibility of setting up a permanent committee in this important field. Two volumes covering the papers presented at the symposia on nuclear metallurgy have been published in low-cost form, and no deficit is anticipated. The Niagara Frontier Section may even publish the proceedings of their forthcoming conference. In addition, the IMD has accepted an invitation from ACTA METALLURGICA to become one of its five sponsoring societies, with the provision that the financial responsibility will not exceed $2,000 per year. Half of this amount will be paid from IMD operating income and half from AIME funds, by approval of the Board of Directors.

The IMD is operated by an executive committee and a number of important standing committees, but their activities and progress are the result of the personal efforts of a large group of its members. Their joint efforts are to be commended since IMD is, today, in the strongest position it has yet reached with the excellence of its programs, publications and financial structure.

EMD Presents First Award for Best Paper

The program of the Extractive Metallurgy Div. at the February 1956 meeting was a fitting climax to a year of hard work on the part of many members, especially those serving on the divisional committees. So many excellent papers were presented, that it was necessary to schedule simultaneous sessions, which meant that those who attended missed at least 50 pct of the technical program.

The problem of scheduling so many papers at the Annual Meeting has given rise to the suggestion that more extractive metallurgy papers be scheduled at regional meetings. This arrangement would also tend to arouse more interest in the division, among the EMD members who do not get to the New York meetings.

Four issues of an EMD Newsletter were printed and mailed during 1955 by the combined efforts of Messrs. Kinnear, Long, and Schlechten, with great assistance from the EMD committee chairmen. Many compliments and encouraging remarks were received from readers, but the editors soon discovered that interesting and appropriate material is hard to find. By common consent it is anticipated that only one or two issues will be attempted in 1956.

During the past year the first EMD Best Paper Award was granted to T. R. A. Davey, formerly at Port Pirie, now employed at the Norddeutsche Affinerie in Hamburg, who contributed two papers to the JOURNAL OF METALS on desilverizing and dezincing lead bullion. The award is financed by a fund to which a number of metal companies contribute through the efforts of T. D. Jones. A committee, with J. D. Sullivan as chairman, worked diligently during the past year to establish the rules and to make the first award.

The technical program at the Annual Meeting featured a wide variety of papers which ranged from those that described details of practice, to others concerned strictly with theory. Likewise, the metals discussed included not only the old standbys of copper, lead, and zinc, but also great attention was given to uranium, titanium, and even newer metals. These papers were gathered by the various committees and finally coordinated by John Kinnear, Jr., who was program chairman in 1955. Under a new arrangement one-third of the membership of each committee is changed each year in an attempt to draw more members into the activities of the division.

The activities of the Division reached a high point with the Annual Stag Luncheon at the Hotel New Yorker on February 22, which had an unexpectedly large attendance including a number of former presidents of the Institute. President Carl Reistle spoke a few words of greeting before the main address which was given by Dean Curtis L. Wilson of the Missouri School of Mines and Metallurgy. Dean Wilson mixed wisdom and humor to the obvious appreciation of his audience. As a final act of business, retiring Chairman A. W. Schlechten turned over the gavel to John C. Kinnear, Jr., EMD Chairman for 1956.

The increased membership in the EMD, and the large number of papers being submitted are evidence of a renewed interest in extractive metallurgy. Large scale production of new metals and the application of

unusual techniques to both new and old metals has stirred up activity to a high degree. MBD members too, are recognizing the importance of hydrometallurgical extractive processes and even IMD members are writing about metal refining.

ISD Reports Most Successful Year

The Blast Furnace Coke Oven and Raw Material Committee, under the chairmanship of Kurt Neustaetter and the National Open Hearth Steel Committee, under Lee Lambing, met in April 1955, at the Bellevue Stratford Hotel in Philadelphia for their 38th conference. The two committees visited Fairless Works, United States Steel Corp. Mr Neustaetter's committee had a record registration of 432 members.

A novel feature of the conference was the successful joint half-day session of the blast furnace and open hearth operators led by Carl Hogberg and Dan Loughrey.

The Bessemer Committee under Arthur Wilder had its most successful year. In the spring of 1955, this committee met for two days in Hamilton, Ontario. The 52 members in attendance, watched the oxygen steel making process at Dominion Foundry & Steel Co. In February 1956 at the Annual Meeting in New York City, the Bessemer Committee held a special luncheon to celebrate the centennial anniversary of the invention of the Bessemer process. All of the bessemer and oxygen steel operators and metallurgists from the U. S. and Canada and several from Europe, were in attendance at this historic function.

The Electric Furnace Steelmaking Committee, with Charles Staley as chairman, held a record breaking meeting in Pittsburgh in December 1955. The Allegheny Ludlum Steel Corp. served as host company for the luncheon and plant visit.

The Physical Chemistry of Steelmaking Committee, under Francis Boulger, fostered many valuable metallurgical sessions at the Annual Meeting and at various conferences and section meetings. This committee is now completing a most worthwhile project—a book on the physical chemistry of electric furnace steelmaking. AIME will publish it in the near future.

The new Mechanical Working Committee, with Michael Tenenbaum as chairman, held its second session at the Annual Meeting in New York. The main feature of the well attended session was the excellent report of drafting practices on primary blooming and slabbing mills compiled from a comprehensive questionnaire covering 85 pct of the primary rolling mills in the U. S. and Canada.

Engineering Library To Exhibit French Books

Some 250 French scientific and technical books will be exhibited at the Engineering Societies Library, 29 West 39 St., N.Y.C. during June 1956. Here engineers, educators, scientists, and researchers will be able to browse through selected books made available by the cultural division of the French Embassy, New York, through the cooperation of the leading publishing firms in France. One of the purposes of the exhibit is to keep American engineers, engineering educators, and researchers informed of the advances made by their French colleagues.

The exhibit will be in the Reading Room of the Engineering Societies Library which will be open Mondays through Saturdays, 10 am to 5 pm during June.

MIT Sponsors June Steel Program

A special two-week summer program on *Metallurgy of Iron and Steelmaking* is scheduled by the Massachusetts Institute of Technology, for June 18-29. Designed as a review for men in this field or for those whose formal education is inadequate for their present needs, this program will study the pertinent basic concepts of thermodynamics and physical chemistry. Laboratory studies of reactions in iron and steelmaking will be described and application of the results discussed. Among the topics to be investigated are heat supply and properties of refractories in furnace construction, and problems with the solidification of steel castings and ingots.

The program will be under the joint direction of John Chipman, head of MIT metallurgy dept., John F. Elliott and Thomas B. King, MIT professors of metal, and F. Denys Richardson of Imperial College in London. Among the guest lecturers from industry are four from U. S. Steel Corp.; and Herbert L. Graham, Jones & Laughlin, Donald C. Hilty, Electro Metallurgical Co., and John S. Marsh, Bethlehem Steel Co.

Registrants for the special summer session may reserve rooms in the Institute's dormitories. All MIT recreational facilities, including the swimming pool and sailing pavilion will be available for their use. Full details and application blanks may be obtained from the Summer Session Office, Room 7-103, MIT, Cambridge 39.

Funds Available From Ordnance Research Office On Application

The Office of Ordnance Research has initiated an application form for those planning to submit proposals for research funds. This form is an outgrowth of material needed by the Office for the administration of its research program. It is also required by university business offices for their records. Individuals interested in undertaking projects in Ordnance basic research, may obtain these application forms by writing to the Office of Ordnance Research, U. S. Army, Box CM, Duke Station, Durham, North Carolina; request Form CS-51.

Regional Reactive Metals Meeting Held in Buffalo

The Regional Reactive Metals Conference, sponsored by the Niagara Frontier Section, was held at Hotel Statler, Buffalo, March 19 through 21, with an attendance of 471. It was the first meeting of its kind anywhere, on the subject of reactive metals. The production, properties, forming, and applications of the *metals of the future*—columbium, tantalum, beryllium, vanadium, rhenium, molybdenum, titanium, and zirconium—were considered in two days of technical sessions. The third day was devoted to plant visits to the Metals Research Laboratories of Electro Metallurgical Co. at Niagara Falls and the Cornell Aeronautical Laboratory in Buffalo.

One of the features of the three-day meeting was the banquet held on Tuesday evening, March 20. Unfortunately, the scheduled speaker, Willy Ley, well known rocket expert, was unable to be present because of illness. A. B. Kinzel, vice president research, Union Carbide and Carbon Corp., spoke in his place on *Research—A State of Mind*. Dr. Kinzel stated that a good research man must have these qualities: personal integrity; ability to concentrate with an all-absorbing interest in the subject; ability to sift facts; courage to persevere when the going is rough; and faith to continue although the road ahead is not clear. Within the researcher's mind there must be dissatisfaction—a problem. The research man first collects all the facts, rearranges them in all possible permutations and combinations, attempting to find a solution. He then starts experimentation in order to check the facts. His subconscious mind goes to work and the conscious mind may bring forth the solution. If not, then more experimentation is necessary before the answer is reached. This pattern of thought, essential to the research man, is in fact, essential for success in any field of endeavor.

Serving as toastmaster at the dinner was the Honorable William B. Lawless, president of the Council of the City of Buffalo.

Chairmen of the various committees arranging the Conference and contributing to its success were: General Conference Chairman, D. C. Hilty; Administration and Finance Committee, C. W. Hart; Exhibits Committee, C. W. F. Jacobs; Local Arrangements Committee, H. J. Cutler; Publicity Committee, G. L. Cox; Registration Committee, D. L. Clark; Program Committee, R. W. Fountain; Attendance and Section Co-ordinating Committee, F. J. Shortsleeve; and Plant Visitation Committee, L. W. Smith.

Pinch-hit speaker for absent Willy Ley was A. B. Kinzel (center) flanked at left by toastmaster William B. Lawless; at right by Walter A. Dean, AIME Vice President.

The Monday evening panel discussion on reactive metals in atomic energy, included experts Frank Foote, Benjamin Lustman, moderator John Chipman and, Harley A. Wilhelm.

There was much activity at the Membership Committee booth where new members were solicited from among those attending who wore blue-bordered badges.

Gordon Research Conference Announced For June 11 to August 31 in New Hampshire

New Hampshire will be the site of the 1956 Gordon Research Conference of the American Association for the Advancement of Science, to be held from June 11 to August 31. The meetings will take place simultaneously at Colby Junior College, New London, New Hampton School and Kimball Union Academy at Meriden.

Established to stimulate research in universities, research foundations and industrial labs, the conferences work toward this end by offering an informal type of meeting with lectures, and free discussion groups.

The program's purpose is not to review the known fields of chemistry. Instead, it brings experts up-to-date on the latest developments, tries to analyze new trends and to provoke suggestions about underlying theories and profitable methods of approach to achieve progress.

Two meetings will be of particular interest to metallurgists. From June 18-22, the New Hampton conference will deal with Metals at High Temperatures. W. Hibbard will be chairman of the discussion on Creep Deformation, while G. J. Dienes will lead the talks on Grain Boundaries, Fracture. Strength of Materials will be the topic chaired by N. J. Grant. The investigation of Oxidation will be led by J. Frye, and C. E. Birchenall will deal with the Growth of Oxides on Metals and Alloys.

From July 23-27, Chemistry and Physics of Metals will be under scrutiny at New Hampton. Equilibria of solid gas, liquid alloy and slag metal are scheduled for discussion.

Those planning to attend are requested to send applications to the director, stating the institution or company with which they are connected and the type of work in which they are interested. Attendance at each conference is limited to 100. Information may be obtained from W. George Parks, director, Dept. of Chemistry, Univ. of Rhode Island, Kingston, R. I. After June 11, address inquiries to Colby Jr. College, New London, N. H.

AIME Adopts New Seal

With the adoption of the new name of the Institute, including the word *Petroleum*, it has seemed desirable to design a new emblem, shown on p. 449 of this issue. The crossed hammers have been the symbol of mining and metallurgy for hundreds of years, and long before oil was discovered in quantity. The new design includes something characteristic of the petroleum industry as well. The new emblems are expected to be available early in the summer, at which time members will be advised. The price will probably be the same as for the former pin, $4 plus 10 pct tax. The emblem will be available as a pin, lapel button, or tie clasp.

MISTAKEN IDENTITY

The picture of the Metals Branch award winners on the top right of p. 467 in the annual meeting story, JOURNAL OF METALS, April, 1956, incorrectly identified **Otwin Cuscoleca** as second from left. The caption should have read **Andre Guinier.**

Bessemer Search Begins

A search is on for the oldest steel blower living in the United States. In this, the year of the Bessemer Centennial, the Bessemer Steel Committee of AIME would like to give appropriate recognition to such an individual. So far, the oldest candidate worked in a bessemer plant in 1882. If you can do better than this, please send the name of your candidate and details to A. B. Wilder, Chairman, Bessemer Steel Committee, c/o National Tube Div., U. S. Steel Corp., Pittsburgh.

Lack of facilities will preclude any exhibits by industrial companies at the Annual Meeting in New Orleans next February.

Round Up Time

A.I.M.E. MEMBERSHIP... IS A MUST.

~ A.I.M.E. IS YOUR PROFESSIONAL SOCIETY ~

When round up time comes around, out in the cattle country, all hands pitch in and the work is quickly and effectively completed. When all the cattle are in, those already branded and in good shape are cut out, and particular attention is paid to the strays and the dogies.

We've had our round-up in New York. But what about the strays and the dogies?

The strays are those members of our profession, our associates who haven't been branded as members of AIME. Everyone of us, by looking around, can find many of these who could be brought into the fold. By giving us their names and addresses, you can help the Membership Committee in their work. While you are at it, you can do a little selling on what AIME has done for you and what it means to you, just to steer them to the corral.

The dogies are our recent graduates who, on January 1st, were automatically transferred to Junior Membership. There will be a new crop soon; graduation day 1956 is fast approaching. There are also Junior Members who reached the age where they are transferred to Associate Membership. Why not extend to them the hand of friendship which has characterized our profession. We need these younger men; they are the leaders of the future.

So why not imitate **Mr. AIMEable,** the *Symbol* of your Membership Committee? Mount your trusty *Cayuse*, get out your lariat, and help us rope them in. This is round up time.

*C. E. Golson**

* *Chairman, AIME National Membership Committee.*

Around the Sections

• Defying superstition, the **St. Louis Section** held a dinner-meeting on Friday April 13 at the Hotel York in St. Louis. Featured speaker was L. M. Pidgeon, head of the dept. of metallurgical engineering at the University of Toronto, Canada. Dr. Pidgeon addressed the group on *Future Trends in Reactive Metal Production*. A member of CIM, he has been on the staff of the National Research Council of Canada where he worked on electrochemical problems, and was research director for Dominion Magnesium, Ltd.

• The Connecticut Light & Power Co. Auditorium in Waterbury, Conn., was the scene of the **Connecticut Section** meeting on March 14, 1956. Thirty-three members and guests were present.

William E. Milligan, Section Chairman presided until the new slate of officers was elected. They are: Albert I. Blank, Chairman; Delmar E. Trout, Vice Chairman; A. Clyde Wilhelm, Jr., Secretary-Treasurer; and as committee chairmen, Richard M. Treco, Publicity; and James H. Mohr, Membership. George H. Eichelman, Jr. is Member-at-Large.

First speaker of the evening was C. Reginald Marsland, plant metallurgist, Handy & Harman Co., Fairfield, Conn., who discussed the *Production of Silver Alloy Sheet and Strip from Metal Powders*. George W. Cleveland, research metallurgist, Bridgeport Brass Co., Bridgeport, Conn., spoke on the *Production of Welded Aluminum Tube*. The concluding lecture was presented by Lloyd E. Raymond, metallurgist for Singer Manufacturing Co. in Bridgeport, Conn. Mr. Raymond detailed the *Steam Oxidation of Steel*, explaining the advantages of this technique of producing the black oxide coating on steel, over that employing caustic salts.

• The **Washington, D. C. Section** held a dinner meeting on March 6 at the Cosmos Club. Guest speaker was John Garrett, executive secretary, Co-ordinating Committee on Materials, Dept. of Defense. Mr. Garrett addressed the group on the topic of titanium metal. His talk was followed by a film on the mining and processing of ilmenite.

• The annual technical meeting of the **Lehigh Valley Section** was held on Friday, March 30 at 7 pm. Members and guests who convened at the Hotel Bethlehem in Bethlehem, heard Morris Bradley, manager of public relations for M. A. Hanna Co., discuss Labrador iron ore, from development to production. Mr. Bradley illustrated his lecture with films.

• The **Carlsbad Potash Section** was host to the **El Paso Metals Section** on March 27, 1956, for a dinner-meeting at the Riverside Country Club in Carlsbad, N. M. Featured speaker for the evening was A. M. Gaudin, of Massachusetts Institute of Technology who addressed the groups on the subject of *The Leaching of Uranium*.

• The **El Paso Metals Section** met on March 14, 1956 in the Mirror Room of the Hotel Cortez, El Paso, Texas.

Featured speaker at the dinner meeting was C. C. Homan, Jr., assistant chief engineer, El Paso Natural Gas Co., who discussed his company and its subsidiaries.

• A new local section has been carved out of territory formerly in the area of the Delta Section. It will be known as the **Evangeline Section,** and comprises the following Louisiana parishes: Vermillion, Jefferson Davis, Allen, Evangeline, Acadia, Lafayette, St. Landry, Pointe Coupee, St. Martin, West Baton Rouge, Iberville, and Iberia. Chairman of the new section is Drew Cornell. D. D. Jones is Secretary.

The Metals and Mining Groups of the **Philadelphia Section** held a joint meeting on March 29, 1956, at the Lenape Club. The meeting was preceded by a cocktail hour.

W. C. Mearns, of the International Nickel Co., presented a 45-min color movie on *Mining for Nickel*. This film presented a comprehensive view of the modern techniques employed in the mining of nickel ores at Sudbury. This film started with illustrations of modern exploration methods, and then showed clearly, six different techniques for removing the ores.

A very enjoyable and informative question period followed the film.

• The **Northern Ohio Section** enjoyed a record breaking attendance of 325 at their annual off-the-record technical session, March 6, at the Hotel Pick-Ohio in Youngstown. Ervin Wentz, U. S. Steel Corp., and Robert P. Hill of Sharon Steel Corp. were co-chairmen of the successful meeting, jointly sponsored by NOHC and Bessemer Steel Committee.

James W. Tyssee, safety manager, Republic Steel Corp., addressed the group, emphasizing the need for management's alertness to unsafe practices which can be altered before accidents occur. L. G. Ekholm, U. S. Steel, followed with a film on ingot mould castings. Then John Stukel, Youngstown Sheet & Tube Co., described future trends in pneumatic processes. The concluding speaker, F. C. Muttitt, Algoma Steel Corp., Ont., Canada, detailed experiments made at his plant using basic brick in checkers.

Toastmaster for the Fellowship Dinner, Joseph Turner, introduced the featured speaker, T. P. Gresham, president of Bethany College, W. Va. Dr. Gresham suggested that, to be effective in a business organization, a man must have four needs fulfilled; ego satisfaction, recognition and appreciation from associates, gratification of esthetic, moral and intellectual needs.

James Smith, new section chairman, served as host for the annual meeting. He was assisted by John F. Beale, the newly elected secretary-treasurer.

• The **Ohio Valley Section** has started a physical metallurgy seminar, (six-week Spring session beginning April 17th) on *Mechanical Metallurgy*. Sessions are held on Tuesdays at 5:15 pm in the auditorium at Battelle Memorial Institute.

A new sound color film on *Ductile Cast Iron* is being offered for technical society meetings, by International Nickel Co. The 16 mm movie runs 16 min and shows the microstructure of ductile cast iron in which graphite occurs in spheroids instead of flake form. The limits of stress and strain for this iron are charted by graph and its mechanical properties, similar to steel, are shown through a series of tests.

Prints of the film are free, except for shipping costs, and should be of special interest to AIME regional sections. Bookings can be made through Rothacker Inc., 729 Seventh Ave., or International Nickel Co., Inc., 67 Wall St., both in N.Y.C.

Long Range Planning Committee Report

The Long Range Planning Committee report has been received by the Board of Directors for consideration at the June Board of Directors meeting. Action on the report has not been taken.

The report will be published in the June issue of JOURNAL OF METALS. Copies of the report are now available upon request from AIME headquarters.

Personals

JAMES M. COPELAND

James M. Copeland was recently named senior project metallurgist by the International Business Machines Corp. A member of IBM since 1951, Mr. Copeland is a native of Portland, Ore. He studied at the University of Washington, the Colorado School of Mines, and Stevens Institute of Technology.

Albert E. Forster was elected chairman of the board of directors, Hercules Powder Co. He succeeds **Anson B. Nixon** who retired but will remain on the board. Mr. Forster was elected president of the company in 1953. Re-elected vice presidents were: **Wyly M. Billing, John J. B. Fulenwider, John B. Johnson, John R. L. Johnson, Jr., Edward B. Murrow** and **Philip B. Stull.**

Arthur F. Kohn, Jr. has been promoted from superintendent of the Los Angeles plant to assistant to the general manager of the Federated Metals Div., American Smelting & Refining Co., with headquarters in Perth Amboy, N. J. Mr. Kohn joined the company in 1935, a year after graduating from the University of Michigan. He has worked at the Chicago and Whiting, Ind., ASARCO plants. Additional appointments in the Federated Metals Div. are: **B. E. Anderson,** chief engineer, Salt Lake City; and **Robert Dean Mathis,** superintendent of the Los Angeles plant.

Eric B. T. Kindquist is the new president of Everite Co. Inc., in Brooklyn. He was formerly vice president and general manager Garfield Wire Div., Overlakes Corp., Garfield, N. J.

Carl K. Stewart, formerly with the International Nickel Co. is now senior metallurgist for the Curtiss-Wright Corp., N. J.

Eugene J. Lenar has joined the Dodge Steel Co. in Philadelphia. Previously Mr. Lenar was chief metallurgist for West Michigan Steel Foundry Co. in Muskegon, Mich.

Fred H. Johnson has been promoted to engineering consultant to the vice president, Inland Steel Co., Chicago, from his post as chief engineer in the company.

Blair L. Sackett has retired as metallurgical manager of Tooele smelter operations, International Smelting & Refining Co., in Salt Lake City, a subsidiary of Anaconda Co. A member of the firm since 1912, Mr. Sackett also served as consultant for their exploration dept. He is succeeded by **Carlos Bardwell** who was superintendent of the Tooele plant. Mr. Bardwell joined Anaconda-International 43 years ago, after receiving his B.S. degree in chemical engineering from the University of Utah. Both men are former chairmen of AIME's Utah section.

Other company promotions are: **G. A. Burt,** assistant metallurgical manager, Salt Lake City; **W. J. McKenna,** general superintendent at Tooele; **E. W. Steinbach,** assistant general superintendent; and **T. W. Saylor,** lead plant superintendent.

THOMAS K. GRAHAM

Thomas K. Graham has been appointed manager of the Raritan Copper Works, International Smelting & Refining Co., at Perth Amboy, N. J. He succeeds **Lorin W. Kemp** who is retiring after 42 years of service with Anaconda, the parent company. A graduate of Massachusetts Institute of Technology, Mr. Graham began in the research department of Anaconda, Montana, transferring to the reduction works in 1936 where he has served till now.

William C. Aitkenhead was chosen by the United Nations to make a four-month study of electrolytic zinc refining methods in Yugoslavia. Dr. Aitkenhead, an internationally known metallurgist, is on leave from Washington State College where he is head of the mining experiment station. He left last month to serve as technical expert under the

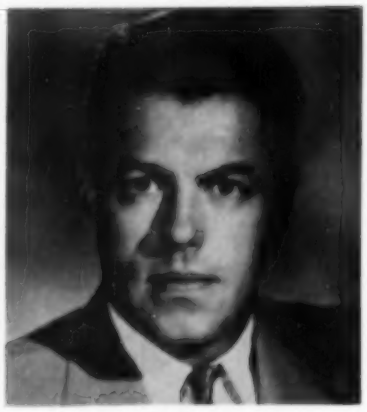
WILLIAM C. AITKENHEAD

expanded technical assistance program of the UN. A few years ago Dr. Aitkenhead made preliminary tests on zinc ore from the Trepca Mines in Yugoslavia, which will be processed in the large chemical and metallurgical center now under construction, near Belgrade. After completing this assignment in Yugoslavia, Dr. Aitkenhead will visit Italy and Sardinia to study the processing of oxidized zinc ore there.

Ihsan - Ul - Haq Chaudri, formerly chemical examiner in Lahore, Pakistan, is now pilot officer at R.A.F. Technical College in Henlow, U. K.

Robert G. Thompson has been promoted to chief of the raw materials engineering div., U. S. Steel Corp.'s applied research laboratory in Monroeville, Pa. Mr. Thompson was formerly employed as a research associate for the company's research and development laboratory in Pittsburgh.

Thomas Drever has been re-elected to the board of directors of American Steel Foundries for a three-year term. A member of the company since 1910, Mr. Drever expressed the wish to be less active and, therefore, was not re-elected as chairman of the board. He will continue, however, to serve the company in a consulting capacity.



LLOYD A. AMOS

Lloyd A. Amos has been appointed works manager of Kaiser Aluminum & Chemical Corp.'s new plants at Ravenswood, W. Va. A veteran of 20 years in the aluminum industry, Mr. Amos was named manager of Mead Works in Washington, last year. Prior to that, he served in the same capacity for two years at the Chalmette, La., reduction plant. He will be succeeded at Mead Works, by **A. F. Garcia,** formerly manager of process control at the company's plant in Oakland, Calif.

Robert L. Duffner, formerly engineer with the Hudson Wire Co., Ossining, N. Y., is now associated with the Anaconda Wire & Cable Co., Hastings on the Hudson, N. Y.

Kenneth L. Keating has joined the semiconductor products div. of Motorola Inc. in Phoenix, Ariz. Dr. Keating was formerly a metallurgist with the Bell Telephone Laboratories in Allentown, Pa.

George V. Slottman was honored by the International Acetylene Assn. for his scientific contributions to carbide, acetylene, and oxygen technology. On March 13, 1956 Dr. Slottman was presented with the Morehead Medal for 1955 at the annual dinner of the association held at the Hotel Statler in Los Angeles. The dinner was the highlight of the three-day annual convention which featured technical, education, and special application sessions. A member of AIME, Dr. Slottman is vice president and director of research, Air Reduction Co. Inc. in New York.

Edward R. Weidlein was given a testimonial dinner in Pittsburgh on March 19, by members of the Mellon Institute of Industrial Research, on the occasion of his retirement as president of the institute. Dr. Weidlein, who is approaching 69, has departed on a federal government mission abroad. Following his return to Pittsburgh, he will continue to serve the institute as a member of the board of trustees.

H. N. Lander has been named development engineer, process metallurgy, at Jones & Laughlin Steel Corp., Pittsburgh. Dr. Lander was formerly employed in the research dept. of Metal Hydrides Inc., Beverly, Mass. He received a D.Sc. degree in 1955 from the Massachusetts Institute of Technology where he also completed his undergraduate studies.

Other appointments in the company's technical services division include: **A. W. Gessner** and **Earle F. Young, Jr.,** who have joined the chemical engineering services as process engineers; and **G. H. Enzian** who has been promoted to assistant director of this division. Previously, Dr. Gessner, a native of Berlin, was employed by the Chemische Werke Huls in Germany. Mr. Young has

G. H. ENZIAN

worked for Babcock & Wilcox Co. in Ohio, and is co-author of *C.E. Refresher Series—Kinetics in Reactor Design* which will appear in *Chemical Engineering* Magazine. Jones & Laughlin have also announced the election of C. H. Bradley, of Indianapolis, to their board of directors.

Louis A. Carapella has been appointed director of product research, metal division, research and development dept., Continental Can Co. Inc., Chicago. Prior to accepting this post, Dr. Carapella was section manager, atomic power division, Westinghouse Electric Corp., Pittsburgh.

Kenneth W. McEuen, formerly chief metallurgist with J. Bishop & Co., platinum works, Malvern, Pa., has joined Lukens Steel Co., Coatsville, Pa., as a research engineer.

George M. Lee, metallurgical engineer with Ventures Ltd., Toronto, Canada, has been transferred to British East Africa, where he will be associated with the company's Kilembe Mine in Uganda, which produces copper and cobalt.

Paul E. Mueller has joined Kaiser Aluminum & Chemical Corp. in Halethorpe, Md., where he will be employed as a remelt metallurgist.

Gerald J. Grott has been named general manager of Airloy Inc., with headquarters in Ennis, Texas. Prior to assuming this post. Mr. Grott was with Unitcast Corp., Toledo.

Edwin Tankins has joined the faculty of the University of Pennsylvania, in the dept. of metallurgy. Mr. Tankins was formerly with Westinghouse Electric Corp., steam division, in the metallurgical engineering section, Pittsburgh.

Edward E. Reynolds has been promoted to associate director of research at Allegheny Ludlum Steel Corp., Watervliet, N. Y.

John G. Dean, chemical and metallurgical consultant, has been retained by Climax Molybdenum Co., in N. Y., to advise on the company's expanded chemical program. This will include development of new applications for molybdenum compounds in catalysis, lubrication, agriculture, and pigments, as well as research into other fields where molybdenum chemicals are of potential value. Dr. Dean, is consultant to several large chemical and metal companies and is on leave from Columbia University where he is director of the Div. of Cooperative Research in the School of Engineering. Previously he was supervisor of research and development for International Nickel Co.

FRANZ L. MAYER

Franz L. Mayer has left the Tin Processing Corp. in Texas City, Texas, where he was employed as a research engineer. Mr. Mayer is now associated with the Chilex Exploration Co. in Chuquicamata, Chile, as a metallurgical chemist.

Gaylord T. Stowe, formerly assistant vice president, E. J. Lavino & Co., has been named vice president in charge of refractory sales and engineering. He succeeds **Raymond E. Griffith** who retired but will continue on the board of directors of the company.

D. R. Bell has been appointed to the physical metallurgy div. of the U. S. Bureau of Mines and is also technical surveyor for the Federal Government in Canada. Prior to this, Mr. Bell was a metallurgical engineer for the Steel Co. of Canada Ltd.

Everett H. Belter, formerly with the Columbia Gas System Service Corp., is now project assistant at the University of Wisconsin, Madison, Wisc.

Raymond L. Walsh, assistant vice president and chief engineer of Universal Atlas Cement Co. has retired after 30 years service but will be retained in a consulting capacity. He is succeeded by **Chester D. Rugen** who has been appointed assistant vice president-engineering and **Robert B. Jordan** as chief engineer. Mr. Walsh first joined the Chicago branch of Universal Atlas as assistant electrical engineer and became chief engineer, N. Y. in 1953. A native of Chicago, he graduated from Illinois Institute of Technology and holds membership in the AIEE and the Assn. of Iron & Steel Engineers.

A member of the engineering department since 1930, Mr. Rugen became operating engineer in 1942 and was promoted to assistant chief engineer in 1953. He has worked in all of the company's plants, specializing in plant machinery and equipment. Born in Glenview, Ill., Mr. Rugen is a graduate of Purdue University. A member of AIME, he has served on committees relating to the cement industry.

Mr. Jordan, who began his career in 1937 at the Chicago South Works of the Steel Corp., became chief construction engineer of Fairless Works, Pa. in 1951. There he was in charge of construction for all sheet, tin and rolling mill facilities. He has been assistant chief engineer at Universal Atlas since 1953. A native of Chicago, he attended University of Illinois and is a graduate of Illinois Institute of Technology. He is a member of the Western Society of Engineers, Pennsylvania Society of Professional Engineers and the Blast Furnace & Coke Assn.

Jack M. Noy is research director at the Quebec Iron & Titanium Corp., in Sorel, Que., Canada. Mr. Noy previously was a plant metallurgist with the Climax Uranium Co., Grand Junction, Colo.

E. J. Kauffmann, Sr. has retired as vice president of Valley Mould & Iron Corp., Hubbard, Ohio. Now residing in Girard, Ohio, Mr. Kauffmann will serve the company as consultant.

Peter W. Leidich, formerly assistant manager of mining engineering at Kaiser Steel, Eagle Mt., Calif., has joined the Pima Mining Co. in Tucson, Ariz., as assistant resident manager.

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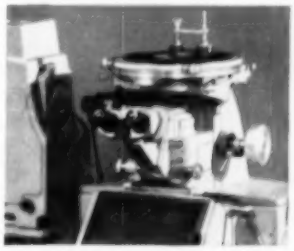

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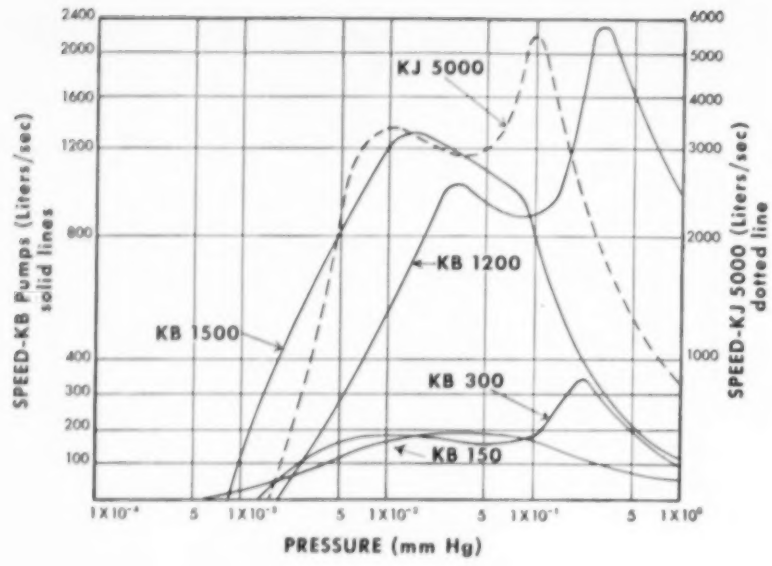

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Bernard L. Jones has been promoted to the newly created position of chief engineer at Crucible Steel Co. of America, Pittsburgh. **Tore Wallin** has been named assistant chief engineer. Mr. Jones began his career in 1925 with the U. S. Steel Corp. in Chicago. Since then he has been engaged in planning steel plants for developments in Russia, Israel, Egypt and Central European countries, as well as the U. S. Prior to joining Crucible in 1950, Mr. Jones was employed by the Inland Steel Co., Ind., for ten years. A native of Nova Scotia, he attended the University of Illinois and is a member of the Assn. of Iron & Steel Engineers.

Mr. Wallin has been with the company since 1923, and was appointed planning and development engineer in 1953. He was born in Sweden and was educated at Orebro Technical Institute there, receiving his degree in chemical engineering. Mr. Wallin is a member of the Professional Engineers' Society and the Engineer's Society of Western Pennsylvania.

Fred R. Kyle has joined Republic Steel Co. in Cleveland. Mr. Kyle was formerly employed by the Inland Steel Co. of Chicago.

Dillon Evers has left the academic world to join the Mallory-Sharon Titanium Corp. in Niles, Ohio. He was formerly associate professor of metallurgical engineering at Purdue University, Lafayette, Indiana.

DILLON EVERS

Robert S. Miltenberger has resigned as engineer in the research dept. of Bethlehem Steel Co., Bethlehem, to join U. S. Steel Corp., Chicago.

H. W. Franz, who was chief metallurgist for Nickel Processing Corp. in Nicaro, Cuba, has joined the research center of Kennecott Copper Corp. in Salt Lake City, as project development engineer.

Eric Gregory has crossed the Atlantic to accept a post with the Sintercast Corp. of America in Yonkers, N. Y. Mr. Gregory was associated with the Manganese Bronze & Brass Co. Ltd. as a metallurgist at Elton Park Works, Ipswich, Suffolk, Eng.

Obituaries

Heath McClung Steele

An Appreciation by
Harold K. Hochschild

Heath McClung Steele (Member 1922) died in New York City on Feb. 21 at the age of 71. He had been in poor health for about two years.

Born in Knoxville, Tennessee, in 1884, Mr. Steele was educated at the Baker-Himmel School and the University of Tennessee. After practical mining experience in Tennessee, Virginia, and Nevada, he became associated with J. R. Finlay in 1911 as consulting engineer, with headquarters in New York. In 1917 Mr. Steele joined The American Metal Co. Ltd., and soon afterwards took charge of its Mexican operations. In 1923 he became a director of the company, in New York, and in 1930 was elected vice president. He occupied both offices until his retirement at the end of 1954. Mr. Steele was also president of the Cía Minera de Penoles, S. A., and Cía Metalurgia de Penoles, S. A., in Monterrey, Mexico; Southwest Potash Corp., Carlsbad, N. M., and an officer and director of other subsidiaries of The American Metal Co., as well as a director of the Rhodesian enterprises in which the Metal Co. is interested. He was also chairman of the Tsumeb Corp. Ltd., Tsumeb, S. W. Africa, from its organization in 1947 until his retirement in 1954.

During World War II Mr. Steele served as chief of the aluminum-magnesium division, Bauxite-Alumina Branch, Office of Production Management, in Washington.

Mr. Steele's imaginative leadership contributed substantially to the growth of the Metal Co. He played a large part in the evolution of the company's operations in Mexico and of its copper and by-product refinery at Carteret, N. J. The development of the Pecos Mine can be attributed to his initiative. Owned jointly by the Metal Co. and David M. Goodrich and associates, the mine became a large producer of zinc and lead during the 1920's and 1930's. Mr. Steele was primarily responsible for the company's potash enterprise at Carlsbad, N. M., and for the exploration program which led to their discovery in 1954 of the lead-zinc-copper-silver orebodies in New Brunswick, Canada, which have since been named in his honor.

After his retirement Mr. Steele lived at Glen Mary Farms, Great Mills, Md. Surviving are his wife, Florence Truman Steele; his daughter, Mrs. Sheridan Fahnestock; two sons, Heath Warren and David Truman; five grandchildren; and his sister, Mrs. Henry Clay Long.

Arthur Glenn McKee (Member 1912) died on Feb. 19, 1956 in Cleveland. Born 1871 in Pennsylvania, Mr. McKee studied at Pennsylvania State College and received his B.S. in 1891, at which time he joined General Electric Co. Returning to Penn State he earned his graduate degree in mechanical engineering in 1895, and then joined the H. C. Frick Coke Co. in Pa. as an engineer. From there he went to Carnegie Steel Co., and American Steel & Wire Co. In 1905 Mr. McKee opened his own office as consultant. Not long afterward, it was incorporated as Arthur G. McKee & Co. of which he was president until 1946. From then up to the time of his death he was director and chairman of its advisory committee. The inventor of the McKee revolving distributor, which revolutionized the charging of blast furnaces, he lived to see it used throughout the world. Mr. McKee was a member of the following organizations: AIME, AISI, ASME, the Eastern States Blast Furnace & Coke Assn. and the British Iron & Steel Institute.

Proposed for Membership
— Metals Branch AIME —

Total AIME membership on Apr. 30, 1956 was 24,309; in addition 2,596 Student Associates were enrolled.

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R. B. Caples, Chairman; F. A. Ayer, Vice-Chairman; A. C. Brinker, R. H. Dickson, C. R. Dodson, R. B. Fulton, T. D. Jones, F. W. Hanson, Sidney Rolle, F. T. Sisco, O. B. J. Fraser, F. W. McQuiston, Jr., A. R. Lytle, L. P. Warriner.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire us members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

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Dwayne L. Day, Las Vegas, Nev.
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Edgar E. Fletcher, Columbus, Ohio
Theodore W. Sproull, Cincinnati
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REINSTATEMENT—CHANGE OF STATUS

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Runyon G. Ernst, Woodbridge, N. J.
George B. Guillotte, Salt Lake City
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Meherwan C. Irani, Pittsburgh

Student to Member

Gurdon M. Butler, Jr., Niagara Falls, N. Y.
Robert L. Cleveland, Buffalo
Armin F. Fick, Downers Grove, Ill.
David Goldstein, Drexel Hill, Pa.
Jan S. Jacobi, La Oroya, Peru
George J. Salvaggio, Pittsburgh
Robert W. Wilks, Malvern, Ark.

Student to Junior

John D. Eichenberg, Pittsburgh

Necrology

Date Elected	Name	Date of Death
1932	Walter D. Abel	Aug. 17, 1955
1905	Arthur Howe Carpenter	Mar. 20, 1956
1899	T. R. Drummond	Feb. 28, 1956
1900	Daniel C. Jackling	Mar. 13, 1956
1950	Harry E. Kamprath	Mar. 15, 1956
1920	H. S. Lyne	Feb. 24, 1956
1912	Arthur G. McKee	Feb. 19, 1956
1931	H. C. Miller	Dec. 18, 1955
1955	William F. Mosier	Dec. 26, 1955
1913	Russell B. Paul	Mar. 5, 1956
1954	Hollis P. Sawyer	Unknown
1953	Frank W. Stedman	Oct. 6, 1955
1941	Watson Storey	October 1955
1952	William R. Stout	Mar. 10, 1956
1955	Ross M. Stuntz, Jr.	Jan. 18, 1956
1952	Allan Richard Voimar	July 16, 1955
1910	Thor Warner	Jan. 20, 1956
1948	David M. Wright	Mar. 11, 1956

— Coming Events —

May 22-25, Société de Chimie Physique, annual reunion, Paris, France.

May 24, AIME, New York Local Section, Powder Metallurgy Group, joint meeting with Physical Metallurgy Group, Brass Rail Restaurant, New York.

May 25, AIME, Connecticut Section, annual dinner-dance. Roger Smith-Elton Hotel, Waterbury, Conn.

June 3-8, SAE, summer meeting, Hotel Chalfonte-Haddon Hall, Atlantic City, N. J.

June 4-7, Material Handling Institute, show, Public Auditorium, Cleveland.

June 5, AIME, NOHC, Buffalo Section, golf party.

June 13, AIME, NOHC, Pittsburgh Section, golf party, Pittsburgh Field Club.

June 17-25, Fifth World Power Conference, Vienna, Austria.

June 17-22, ASTM, annual meeting, Hotel Chalfonte-Haddon Hall, Atlantic City.

June 22-July 6, International Machine Tool Exhibition, Olympia, London, England.

Aug. 6-8, SAE, West Coast meeting, Mark Hopkins Hotel, San Francisco.

Aug. 23-25, National Council of State Boards of Engineering Examiners, Hotel Statler, Los Angeles.

Sept. 9-12, AIChE, William Penn Hotel, Pittsburgh.

Sept. 16-22, ASTM, Pacific Coast meeting, Statler Hotel, Los Angeles.

Sept. 26-28, AIME, Rocky Mountain Minerals Conference, Salt Lake City.

Oct. 8-10, AIME, IMD fall meeting, Hotel Carter, Cleveland.

Oct. 12, AIME, NOHC Eastern Local Section, annual meeting, Philadelphia.

Oct. 16-18, AIEE, conference on magnetism and magnetic materials, Hotel Statler, Boston.

Oct. 28-Nov. 1, Electrochemical Soc., Statler Hotel, Cleveland.

Nov. 2, AIME, Pittsburgh Local Section, NOHC Pittsburgh Local Section, annual off-the-record meeting, William Penn Hotel, Pittsburgh.

Dec. 5-7, AIME, Electric Furnace Steel Conference, Hotel Morrison, Chicago.

Dec. 9-12, AIChE, annual meeting, Statler Hotel, Boston.

Feb. 24-28, 1957, AIME Annual Meeting, Roosevelt and Jung Hotels, New Orleans.

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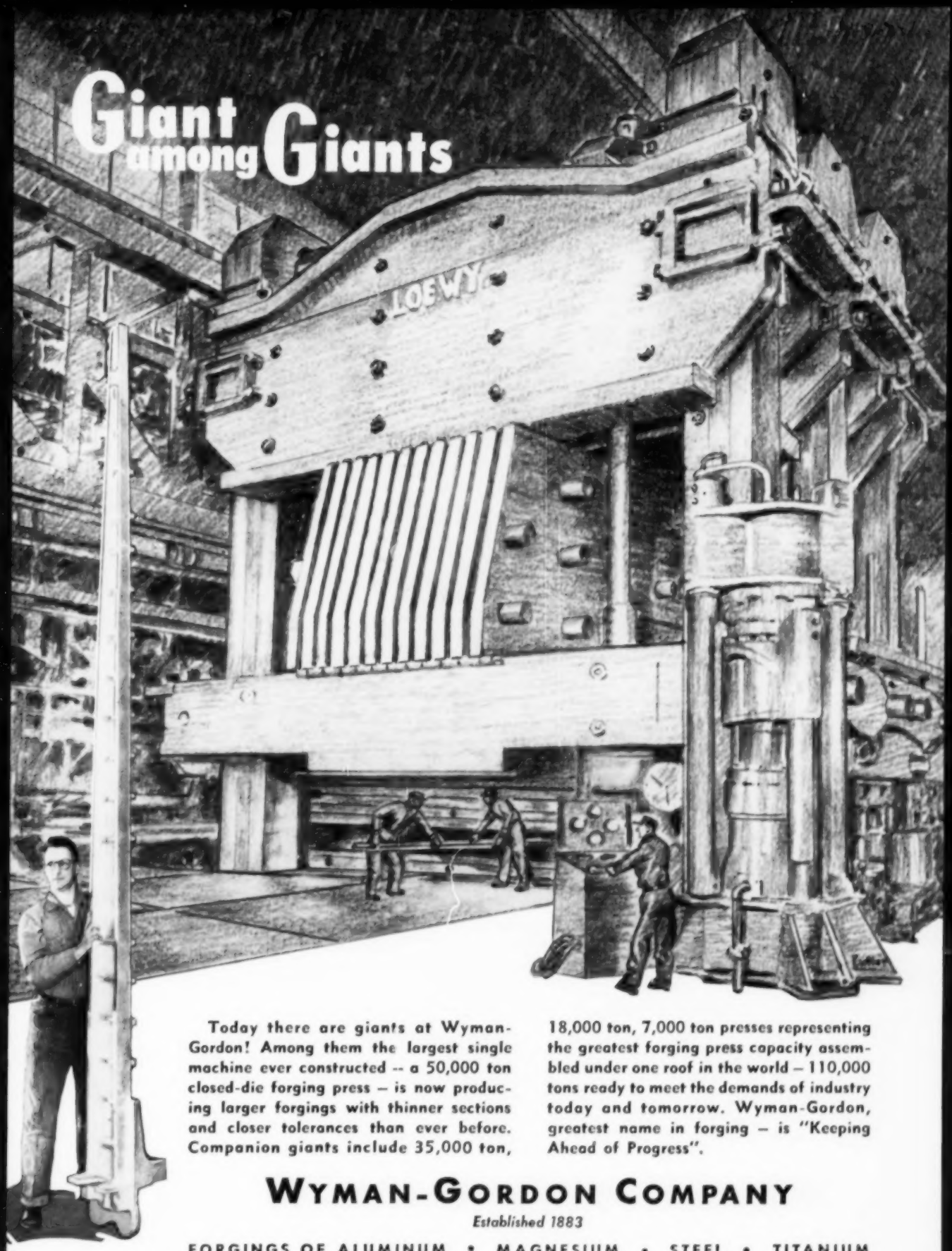

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